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A TREATISE
ON
PHYSICAL CHEMISTRY

VOLUME ONE

A TREATISE

ON

PHYSICAL CHEMISTRY

A Co-operative Effort by a Group of Physical Chemists

EDITED BY

HUGH S. TAYLOR, D.Sc. (Liverpool)
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In Two Volumes, Illustrated

VOLUME ONE

SECOND EDITION

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"It is also true that man sees more of the things themselves when he sees more of their origin; for their origin is a part of them and indeed the most important part of them. Thus they become more extraordinary by being explained. He has more wonder at them but less fear of them; for a thing is really wonderful when it is significant and not when it is insignificant."

G. K. CHESTERTON—"St. Francis of Assisi."

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PREFACE TO THE SECOND EDITION

The reception accorded the first edition of this book was such that a decision had to be reached one year ago as to the advisability of a third printing or a new edition. The rapid developments in several branches of the subject made the decision for a new edition inevitable. A perusal of these volumes will show in what directions progress has been dominant. The chapters dealing with the electrochemistry of solutions, homogeneous and heterogeneous reaction velocities, the applications of the quantum concept to the structure of matter and to photochemistry, the use of statistical mechanical methods in chemistry have all called for extended revision by reason of developments in the five year period which has intervened since the book was first put at the disposal of the advanced student of physical chemistry.

The opportunity thus offered has been taken to present in this edition a more advanced treatment of the kinetic theory of gases and liquids and also a considerably extended discussion of colloidal systems. As a result of all these changes the size of the book has undergone a somewhat considerable increase necessitating a readjustment of the division of chapters, the first chapter (XII) of the second volume of the old edition now becoming the last chapter of the first volume. The order of presentation of the subject matter remains unchanged.

The necessity of writing a preface offers the editor a welcome opportunity to express his gratitude and indebtedness: to his contributors for their renewed co-operation, to the publishers for their generous support of the effort to produce an attractive as well as an instructive volume and to those students of the science who, by their enthusiastic adoption of the first effort, justified the labors involved in the preparation of the present volumes.

HUGH S. TAYLOR.

PRINCETON N. J.
May 1930

PREFACE TO THE FIRST EDITION

An adequate treatment of the subject of modern physical chemistry for the advanced student is a difficult task for any one person. The ever-widening scope of the subject, its extension into domains which, even a decade ago, were as yet unknown or unexplored, demand qualities of broad scholarship on the part of an author which are largely incompatible with the call for specialized endeavor in other phases of his work. The present treatise on physical chemistry represents, therefore, a coöperative effort on the part of a number of physical chemists to cover generally the major portions of their science by contributions in those portions of the subject which their particular inclinations have led them more especially to study and to which they themselves may have contributed by their own effort and research. It is hoped that, in this way, a more authoritative treatment of the several branches of the subject may have been achieved; perhaps, also, a fresher exposition of the subject in its various phases may have been realized. Through coöperation, it should have been possible to secure a more up-to-date record of the present status of the science, since the time consumed in the preparation of such a treatise can obviously be reduced beyond the limits which must be demanded by a single author. Furthermore, where labor is shared a more frequent revision can be more easily achieved.

Coöperation in the present undertaking has been freely and generously given. The editor wishes to express, therefore, his gratitude for such assistance. The responsibility for the plan of the book must rest with him, since his contributors have, in the main, acceded to his requests as to the general trend of their contributions. It will be generally recognized that a new era in physical chemistry is upon us. The science of a decade ago is utterly inadequate to present-day demands. The atom is no longer a philosophical concept but a concrete reality, no longer however "atomic" or indivisible. Energy is considered less and less as a continuum, more and more in units or quanta. The contributions of thermodynamics, of statistical averages, are, more and more, being supplemented by studies of the individual. The classical tradition of physical chemistry was the study of the individual from the behavior of the crowd. Are there not signs that the behavior of the crowd can be deduced from the study of the individual? It is with such thoughts in mind that the plan of the book took shape. Atomistics and kinetics must supplement the general conclusions of statistical and thermodynamic research. The modern student must avail himself alike of all the varied avenues of approach to the unexplored terrain.

The book is addressed primarily to the advanced student in physical chemistry, to the research student desirous of learning the background to his problem and to the research man in industry who requires the theoretical treatment of his practical investigations. Actually, however, the book may have a wider appeal. As divided into two volumes, the work appears to meet

the demand for a graduated text in physical chemistry. The material of the first volume represents that portion of the subject of theoretical chemistry that can with advantage be addressed to the first year student of physical chemistry who plans to continue his studies beyond that year. It contains the main features of the classical era of physico-chemical development. The volume contains, it is true, a more detailed treatment of the subject than the average student will fully grasp in his first year of its study. It will not, however, be amiss for the serious student to find in his text somewhat more than will be discussed in his lectures and exercises. Stimulation to further effort may result. For all students who plan to take more than one year of work in physical chemistry, assimilation of the material of the first volume will represent a very solid accomplishment and a sound basis for approach to the more modern aspects of the subject which find their treatment in the second volume. In the latter, the student is taken to the borderland of the subject where active development is even now in progress.

A coöperative text offers a fruitful field for the critic or reviewer anxious to locate the weaknesses of a text rather than its virtues. To such people it will be well to point out that an editorial survey has resulted in the discovery of many places in the book where duplication occurs and even where apparently divergent views have found expression. Many of these have been carefully considered and discussed with collaborators and colleagues and have been allowed to remain. For, where divergent views are held, there is evidently something lacking in absolute truth of the matter discussed. Such passages may therefore be taken by the student as the signposts to further research and investigation. It is with the hope that these volumes may lead to a fuller investigation of the fundamental theoretical bases upon which all the fine structure of the modern science of chemistry, academic and applied, has of necessity to stand that the labor involved in their preparation has been unremittingly given. Other tasks and endeavors would, doubtless, in many cases have been preferred. The editor gratefully acknowledges the wholehearted coöperation of his contributors and the efforts which they have made to facilitate his work, not only in their own contributions but also in their discussion of the efforts of others. In particular, an expression of gratitude is here made to Dr. T. J. Webb, of Princeton University, who possessed, in large measure, qualities of editorship which the editor himself lacks and who has perused, and criticized, with many valuable suggestions, all of the material included in these volumes. To my brother, Dr. H. Austin Taylor, who has shared generously in the labors of index and proof my thanks are also due. The efforts which the publishers have put forth are revealed in the quality of the printing and the make-up of the book. But, beyond this obvious coöperation, there is a wealth of effort in which their anxiety to surmount difficulties with generosity has been most conspicuous. For this they deserve especial thanks.

HUGH S. TAYLOR.

PRINCETON, N. J.,
July, 1924.

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CHAPTER I

THE ATOMIC CONCEPT OF MATTER

BY HUGH S. TAYLOR, D.Sc.,

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The inception of the modern era in chemical science may be attributed to the proposal of the atomic theory of chemical action by John Dalton in the first volume of his New System of Chemical Philosophy, 1808. The scientific era in which the Daltonian concept was formulated was especially favorable to its development. The theory of atomic constitution was no new theory. The Greek theory of atoms, due to Leucippus and handed down to us in the writings of Democritus, is the first of which we have record. Boyle included in his conception of elementary substances some notions of atomic constituents. Dalton himself was led to the atomic theory by reason of his admiration of the Newtonian doctrine of the atomic constitution of matter. The quantitative era into which Dalton's theory was born provided the circumstances necessary and favorable to its growth. The theory simplified and correlated much that the quantitative spirit had disclosed and had not yet explained. It provided the framework upon which was built the chemical philosophy and the chemical research of the nineteenth century. Towards the close of the century it seemed as though the theory might give way to an interpretation of the science based upon energetics. But, in the new century, it emerged once more, broadened and amplified by the discoveries of sub-atomic phenomena.

The atomic theory of Dalton postulated the existence of minute indivisible particles or atoms, each of equal weight for the same element, atoms of different elements, however, having different weights. Compounds were the result of union of dissimilar atoms the ratio of whose weights was proportional to their combining weights. This fundamental idea of atoms having characteristic weights and combining to form chemical compounds at once illuminated the quantitative facts of chemical combination then known. They may be thus briefly summarized:

(1) *The Law of Definite Proportions*, established experimentally by Proust in 1799. The elements which form a chemical compound are united in it in an invariable ratio by weight, which is characteristic of that compound. Proust's analyses were made with carbonate of copper, artificial and natural, the two oxides of tin and the two sulphides of iron. Proust showed, in contradiction of claims put forward by Berthollet on behalf of variable composition due to mass action, that when a metal combines with oxygen in more than one proportion there is no gradual increment of one element but a sudden, *per saltum*, increment. His analytical work was not sufficiently accurate to establish the law of multiple proportions.

(2) *The Law of Multiple Proportions*, deduced from experimental work by Dalton and formulated by him in conformity with his preconceived atomic theory. When an element

combines with another to form more than one compound the masses of the second element combining with a fixed mass of the first element bear a simple ratio to one another. The accurate analyses of Berzelius provided abundant evidence of the truth of this law which the less accurate efforts of Dalton produced.

(3) *The Law of Reciprocal Proportions*, established by the experimental work of Richter (1792–1794). When two or more elements combine with a third in certain proportions they combine with each other in the same proportions or in multiples of these proportions. In his book *Stoichiometry of the Chemical Elements* published in the above years this law of reciprocal proportions is illustrated.

The Law of Conservation of Mass, formulated by Lavoisier in 1774 upon the basis of experimental measurement, states that the total mass of the reactants in a chemical reaction is equal to the total mass of the products of reaction. All these laws, quantitatively exact and experimentally verifiable, fitted admirably into the framework of chemical principles established by Dalton's Atomic Theory. Further support was quickly forthcoming. Gay Lussac put forward in 1808 his *Law of Combining Volumes*. When gases combine they do so in simple ratios by volumes, the volume of the gaseous product bearing a simple ratio to the volumes of the reactants when measured under the same conditions of temperature and pressure. An attempt by Berzelius to interpret this law in terms of the atomic theory failed owing to a lack of understanding of the differences between atoms and molecules. Knowing, as a result of the earlier investigations of Gay Lussac, that many gases vary similarly when subjected to temperature, and, from the investigations of Boyle, to pressure changes, Berzelius suggested that equal volumes of different gases under like conditions of temperature and pressure contain the same number of atoms.

Avogadro's Hypothesis: The correct correlation of the atomic theory with the characteristics of ideal gases is due to Avogadro who propounded in 1811 the Avogadro hypothesis. Though not accepted by the early proponents of the atomic theory and only commanding general adherence after the exposition of the hypothesis some 47 years later by his fellow countryman the Italian scientist Cannizzaro, the hypothesis of Avogadro was a true exposition of the facts concerning gases. The hypothesis may be stated in the following terms: Equal volumes of different gases under the same conditions of temperature and pressure contain the same number of molecules. The limitations of this hypothesis as regards actual gases and the many experimental methods which have now been developed actually to determine the number of molecules in a given volume of gas will be dealt with in appropriate portions of the following chapters. At this stage it will suffice to indicate the actual change introduced by the Avogadro hypothesis into the Daltonian concept of atoms and atomic combinations. On the Avogadro principle, the atom became the smallest particle which can enter into chemical combination. The molecule became the smallest particle of matter which was capable of independent existence. This distinction clarified the known experimental facts. It explained, for example, how one molecule of hydrogen and one molecule of chlorine combined to form two molecules of hydrogen chloride. Each molecule of hydrogen and chlorine contained two atoms whereas the molecules of hydrogen chloride contained

an atom each of hydrogen and chlorine. It is perhaps advisable to point out, now that the difficulties associated with the terms atom and molecule no longer exist, that the definition of the molecule given above lacks somewhat in rigor. For, we now know that, under proper conditions, not only molecules of diatomic gases such as hydrogen, chlorine and iodine may exist in the free state but that atoms may also so exist provided the conditions of temperature and pressure be suitably chosen. Under such conditions the molecule and the atom become identical.

With the atomic theory as guide, Berzelius proceeded to the determination of atomic weights of a wide variety of elementary substances. The determination involves two steps, (1) the measurement of the combining weight and (2) the finding of the ratio of combining weight to atomic weight. The former is an experimental operation generally involving some kind of quantitative analytical procedure as, for example, the determination of the quantities of potassium and chlorine in unit quantity of potassium chloride, of hydrogen and oxygen in water or of hydrogen and chlorine in hydrogen chloride. From such determinations the combining weights of oxygen, chlorine and potassium in terms of hydrogen as unity may be determined. The second step, however, involves a knowledge of the number of atoms which are combined in a compound with the reference element. Thus, to take an example of historic interest, the atomic weight of oxygen relative to that of hydrogen as unity would be approximately 8 or 16 according as one or two hydrogen atoms combine with one atom of oxygen, the combining weight being 8. It is in the solution of this problem that the Avogadro hypothesis performed a most useful function, delayed, however, by the non-recognition of the importance of the hypothesis until Cannizzaro's demonstration of its utility in such connection. Until that demonstration was given, no general agreement as to atomic weights was possible, different observers using different values which, however, were simple multiples of other values for the same element, according to the preconceived idea of the experimenter as to the atomic ratios prevailing in the compound analyzed.

Dulong and Petit's Law: Two further principles of great utility in deciding doubtful cases of atomic weight values were discovered and employed in the early years of the atomic theory. The one, the law of Dulong and Petit was applicable to solid elementary substances. The law, formulated in 1819, states that the product of the atomic weight and the specific heat is approximately 6 calories. It will be shown that this law is a limiting law applicable to all solid elements under specified conditions. Known exceptions, such as boron and carbon, which show low atomic heats at ordinary temperatures, manifest at those temperatures a phenomenon common to all solid elements if the temperature chosen for the determination be sufficiently low. At higher temperatures, even these elements have atomic heats approximating those demanded by the law. Nevertheless, a sufficiently large number of elements obey the Dulong and Petit relation at ordinary temperatures as to make this principle of important assistance in deciding cases of doubt in reference to atomic weights deduced by other methods.

Isomorphism: The second principle was of assistance in the study of the atomic weights of elements present in crystalline compounds. In 1820 Mitscherlich called attention to the practical identity of crystalline forms of the corresponding salts of phosphoric and arsenic acids. They crystallized with the same molecular quantities of water of crystallization and possessed the power of forming mixed crystals. As a result of such observations, Mitscherlich concluded that analogous elements or groups of elements can replace one another in compounds without material alteration of crystalline form. Two compounds so related were termed isomorphous and the phenomenon was given the name Isomorphism. The identity of form is not absolute. The distance between atoms varies slightly in one compound from that in the compound of the next analogue. These differences persist even in the mixed crystal and result in distortion of the crystal angles. The variation of interatomic distances and the distortion of the crystal angles become greater the more widely divergent are the analogous elements. As a consequence, with the more widely divergent analogues, mixed crystals will not occur even though there is identity of crystal form between the compounds. Substances may crystallize in two or more distinct crystallographic systems having, nevertheless, constant chemical composition. Such behavior is termed dimorphism. If isomorphism occur between the two forms severally of two such dimorphous bodies the bodies are said to be isodimorphous, the phenomenon being, correspondingly, isodimorphism. Similarly, trimorphous substances are known.

From the standpoint of the atomic theory, however, quite apart from the importance of Mitscherlich's observations crystallographically, isomorphism assisted greatly, since it gave a ready indication of chemical composition in the case of substances crystallizing in the same form and isomorphously with substances of known composition. Berzelius made great use of the principle in fixing atomic weights and in checking the results of his analytical investigations. Isomorphism has acquired a still greater range of applicability as the result of more recent deductions concerning the sub-atomic characteristics of the atom. As will be later demonstrated, isomorphism is possible between compounds containing elements which from the Mitscherlich standpoint would not be regarded as analogues but which, from a similarity of sub-atomic components, acquire identity of crystalline form. (See Chapter V.)

Prout's Hypothesis: Philosophically considered, the Daltonian concept of atoms, of differing weights but incapable of subdivision, is not without difficulties. Reason suggests the possibility of subdivision even though technique may not be adequate to its achievement. As a consequence, side by side with the many achievements of theoretical chemistry in the 19th century, based fundamentally upon the atomic theory, there has persisted the essentially opposite viewpoint, namely that of continuity or unity of matter as opposed to the discontinuous view of material substances which the atomic theory postulates. This contrary viewpoint has been developed both consciously and unconsciously. Prout's hypothesis put forward in 1815 is the earliest illustration of conscious development. Prout, reasoning from the approxima-

tion to whole numbers of the atomic weights of several of the elements, suggested that the elements might be, in reality, polymers of hydrogen. This was a revival of the protyle theory of matter with quantitative investigations as its support. But further quantitative study tended to withdraw support from the hypothesis of Prout. The hypothesis gave an added stimulus to exact atomic weight determinations and these but served to demonstrate effectively that many of the atomic weights were markedly divergent from whole numbers. Stas' determinations of atomic weights, and notably that of chlorine, were classical researches, with this divergence from the whole number rule as the decisive result.

Döbereiner's Triads: Attempts at classification of the elements on the basis of similarity of properties are less conscious methods of establishing the essential unity of matter. Thus, Döbereiner's observation, in 1817, that groups of three elements chemically similar, with atomic weights in arithmetic progression, could be compiled, while essentially an attempt at convenient classification, involves, in its fundamentals, an appreciation of a unifying principle. The chemical similarity of, for example, lithium, sodium and potassium, chlorine, bromine and iodine, calcium, strontium and barium, sulphur, selenium and tellurium with the very definite arithmetical relationships of their atomic weights, Na − Li = 16.06, K − Na = 16.1, suggests immediately a fundamental factor common to each group of three and so some unity underlying each group. This aspect of the matter was not, however, emphasized either in Döbereiner's triad system nor in subsequent, more comprehensive, systems of classification.

Faraday's Laws of Electrolysis and the Electrochemical viewpoint. The electrochemical researches of Nicholson and Carlisle, 1800, on the decomposition of water, of Davy on the preparation of potassium, sodium, and other metals 1807–1808, and of Berzelius and Hisinger in Sweden 1803–1807, on the decomposition of neutral salts by the electric current, definitely brought electrochemistry to the fore as an auxiliary to other methods of chemical investigation. Davy's Electrochemical theory of affinity and Berzelius' theory of atomic polarization brought electrochemistry into the domain of theoretical chemistry. Faraday's researches in experimental electricity established quantitatively the relationship between electricity and the atomic weights of the elements. Faraday observed that (Experimental Researches, 505): 'For a constant quantity of electricity, whatever the decomposing conductor may be, whether water, saline solutions, acids, fused bodies or the like, the amount of electrochemical action is also a constant quantity.' Furthermore, with different solutions, the amounts of elementary constituents produced by unit quantity of electricity are proportional to their chemical equivalents. In these two laws the atoms and electricity are for the first time intimately associated. Faraday's ions, transferred through solutions by the agency of the current, were carried in definite amounts, one gram ion for every 96,500 coulombs of electricity. Modified by Grove, 1845, by Williamson in 1851, and by Clausius, 1857, in the sense that the decomposition was not effected by

the current but that the ion carriers must exist in part uncombined, the theory of conduction was given quantitative formulation by Arrhenius, 1887, who then assumed that the extent to which the free ions occurred in solution was deducible from the electrical conductance of the solution as well as from the properties of solutions, at that time entirely disassociated from the electrical properties of solutions, namely, osmotic phenomena, freezing point, boiling point and vapor pressures of solutions. The properties of conducting solutions became a function of the positively and negatively charged ions which they contained. Progress from this point of view to those held today came as a result of the researches of the physicist and the student of radioactive change.

The Periodic System of Classification: Before the contributions of the physics of the atom and of radioactivity were achieved, the chemist had provided himself with a broad and comprehensive system of classification of the elements which, more decisively than hitherto, suggested a fundamental unity of elementary structure, though designed, primarily, to emphasize the interrelation of chemical and physical properties. An effort of de Chancourtois (Vis Tellurique, Classement naturel des Corps Simples, 1862) excited little attention among chemists, though substantially a statement of periodicity of properties with increase of atomic weight. Newland's Law of Octaves, 1864, an arrangement of the elements in groups of eight bringing with each eighth element a repetition of properties like the eighth note of an octave in music, aroused much ridicule and little respect, though essentially the correct formulation of periodicity. It is noteworthy to record that, had Ramsay's discovery of the rare gases of the atmosphere preceded this formulation, the analogy with the musical octave would have been lost; the scoffers would have lacked one of their principal weapons of ridicule. Mendeleeff in 1869 established the same periodicity of properties by arranging the elements in the order of increasing atomic weights. His historic association with the law arises because he employed the periodic law, so discovered, as a powerful instrument of chemical classification and a weapon for prosecuting chemical research.

"When I arranged the elements," he wrote, "according to the magnitude of their atomic weights, beginning with the smallest, it became evident that there exists a kind of periodicity in their properties. I designate by the name periodic law the mutual relations between the properties of the elements and their atomic weights; these relations are applicable to all the elements and have the nature of a periodic function."

Simultaneously, Lothar Meyer in Germany was evolving the same generalization. Meyer was more concerned with the periodic variation in the *physical* properties of the elements as a periodic function of the atomic weights of the elements, his graph of atomic volume plotted against atomic weight demonstrating the same broad periodic relationship which we may now detail as the result of the application of the Mendeleeff principle.

The accompanying table embodies the ideas as laid down by Mendeleeff with the modifications introduced by newer and better data than were available to Mendeleeff and modified also by the additions—especially that of Group O, which comprises the rare gases of the atmosphere—which subsequent

TABLE I

THE PERIODIC TABLE

Periods		Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
Formula of highest oxide		—	R_2O	RO	R_2O_3	RO_2	R_2O_5	R_2O_6	R_2O_7	RO_4
Formula of hydride		—	RH	RH_2	RH_3	RH_4	RH_3	RH_2	RH	—
First short period		He *2* 4.00	H *1* 1.008 Li *3* 6.94	Be *4* 9.1	B *5* 10.9	C *6* 12.00	N *7* 14.01	O *8* 16.00	F *9* 19.0	
Second short period		Ne *10* 20.2	Na *11* 23.00	Mg *12* 24.32	Al *13* 27.1	Si *14* 28.3	P *15* 31.04	S *16* 32.0	Cl *17* 35.46	
First long period	Even Series	A *18* 39.9	K *19* 39.1	Ca *20* 40.07	Sc *21* 45.1	Ti *22* 48.1	V *23* 51.0	Cr *24* 52.0	Mn *25* 54.93	Fe *26* 55.84 Co *27* 58.97 Ni *28* 58.68
	Odd Series		Cu *29* 63.57	Zn *30* 65.37	Ga *31* 70.1	Ge *32* 72.5	As *33* 74.96	Se *34* 79.2	Br *35* 79.92	
Second long period	Even Series	Kr *36* 82.92	Rb *37* 85.45	Sr *38* 87.63	Y *39* 89.33	Zr *40* 90.6	Cb *41* 93.1	Mo *42* 96.0	Ma *43*	Ru *44* 101.7 Rh *45* 102.9 Pd *46* 106.7
	Odd Series		Ag *47* 107.88	Cd *48* 112.4	In *49* 114.8	Sn *50* 118.7	Sb *51* 120.2	Te *52* 127.5	I *53* 126.92	
Third long period	Even Series	Xe *54*	Cs *55* 132.81	Ba *56* 137.37	La *57* 139.0	Ce *58* 140.25				
	Odd Series	130.2		The Rare Earth Elements Pr *59* to Yb *71*						
Fourth long period	Even Series					Hf *72* 179	Ta *73* 181.5	W *74* 184.0	Re *75*	Os *76* 190.9 Ir *77* 193.1 Pt *78* 195.2
	Odd Series		Au *79* 197.2	Hg *80* 200.6	Tl *81* 204.0	Pb *82* 207.2	Bi *83* 208.0	Po *84*	— *85*	
Fifth long period		Rn, An, Tn *86* 222	— *87*	Ra *88* 226	Ac *89*	Th *90* 232.15	UX_2 *91*	U *92* 238.2		

research and discovery have permitted. For convenience in subsequent discussion, the table has been amplified by the insertion of the atomic numbers of the elements as well as the atomic weights. The table is in its essentials, however, identical with that of Mendeleeff. It contains 9 vertical columns or groups and 12 horizontal rows termed series or periods. Hydrogen is in a series by itself. It possesses the properties of the elements of Group I in certain of its compounds, that of Group VII in others.[1] Following hydrogen come two *short periods* of eight elements each, falling naturally into the eight groups from Group O to Group VII, helium to fluorine in the first of these two series, neon to chlorine in the second. Beyond chlorine, the next thirty-six elements fall naturally on the basis of properties into two groups of eighteen, the two first *long periods*, argon to bromine in the first, krypton to iodine in the second. These groups of eighteen show a variation from the two short periods in that three elements in each period, so called transitional elements, iron, cobalt, nickel and ruthenium, rhodium and palladium are grouped together in Group VIII. This arrangement was devised by Mendeleeff as a result of obvious difficulties in placing them in other groups and by reason of their close similarity one to another. By the arrangement indicated, krypton and xenon come into Group O with the other rare gases. The other members of the various groups fall naturally into the classification on the basis of similarity of properties. Mendeleeff arranged the remaining elements in three *long periods* in which there were many gaps, but in which the similarity of chemical and physical properties provided a sure guide for allocation. It is now known, as will be later discussed in detail, that, following the second period of eighteen comes a longer period of thirty-two elements of which the initial element is xenon, the last element, Number 85. This long period is succeeded by an incomplete fragment, seven in number, one of which is yet undiscovered, of which the initial element is the emanation of radium, a gas of the rare gas type, and of which the heaviest known element, uranium, is the last member of the series in so far as they have been discovered. The first long period of thirty-two elements contains a trio of similar elements, osmium, iridium and platinum, as in the groups of eighteen, these being assigned likewise to Group VIII. The rare earth elements are also members of this long period of thirty-two.

The Mendeleeff arrangement brings together, in one group, elements which have general family properties, physical and chemical, which vary gradually from first to last and which resemble one another more closely than do any of the other elements. This similarity and gradual variation suggests some common feature of internal construction or architecture. In the series, or horizontal lines of the table, there is a marked difference from member to member in physical and especially in chemical properties. Thus, for example in the matter of maximum oxide forming capacity, the variation of a series is from an element with no power of combination, the rare gas, through elements with respective oxides R_2O, RO, R_2O_3, RO_2, R_2O_5, R_2O_6, R_2O_7 and in some

[1] H_2O—Na_2O; HCl—NaCl; LiCl—LiH. See: Peters, *Z. anorg. allgem. Chem.*, **131**, 140 (1923). Bardwell, *J. Am. Chem. Soc.*, **44**, 2499 (1922).

cases R_2O_8. Each series, however, more or less resembles the series which preceded it, with one proviso. In the long periods there are two series, the so-called 'odd' and 'even' series. Examination will show that the 'even' series 4, 6 and 8 resemble one another, 5 and 7 also, much more so than do the 'even' series resemble the 'odd.' On the basis of indivisible atoms this factor receives no elucidation. It was merely observed and accepted in the original classification. The explanation must be sought and, as will be shown, is found in the architecture of the atom. As observed above with the oxides, the maximum state of oxidation progressively increases from left to right in a series. It should be observed also that the elements show a minimum valency in hydride formation, rising from 0 to 4 as we pass from a rare gas such as helium to a member of Group IV such as carbon. Beyond Group IV, however, the combining power falls as indicated by the compounds NH_3, OH_2, FH. This factor also lacked elucidation in the original formulation of the periodic law.

The Applications of the Periodic Law: As pointed out by Mendeleeff the periodic law could be employed in: (1) The classification of the elements; (2) The estimation of atomic weights; (3) The prediction of properties of unknown elements; (4) The correction of atomic weights.

(1) In the classification of the elements the periodic arrangement has never been surpassed nor superseded. It is still a most useful and convenient method of classifying the data of inorganic chemistry whether of elements or of compounds.

(2) Mendeleeff assigned to indium an atomic weight of 113.4 on the basis of Winkler's value of 37.8 for the equivalent weight; this makes indium tervalent, gives it place in Group III of the table between cadmium and tin, below gallium, where it fits very well. Specific heat measurements of indium metal confirmed the correctness of this assignment.

(3) Mendeleeff used the table to predict the properties of missing elements in Group III and Group IV akin to boron, aluminium and titanium. The predictions concerning eka-boron, eka-aluminium and eka-silicon were abundantly justified and confirmed in the subsequent discoveries of scandium, gallium and germanium respectively.

(4) Mendeleeff predicted corrections in the atomic weights of osmium, iridium and platinum which gave to them this order rather than that given by the order of atomic weights accepted in 1870 which would have given platinum, iridium, osmium. The periodic law has not, however, always been the successful guide in corrections to accepted atomic weights as will now be discussed.

The Defects of the Periodic Law: On placing elements in the order of atomic weights two outstanding anomalies presented themselves to Mendeleeff. Tellurium, being assigned an atomic weight greater than that of iodine, would have passed into the halogen group, while iodine would have been placed in the oxygen, sulphur, selenium group. This would have been an obvious inversion of the periodicity of properties. Since the atomic weight of iodine had been many times checked and rechecked, so that considerable certainty could be attached to its value, Mendeleeff suggested that the atomic weight of tellurium must be wrong, that the correct value would be between 123 and 126 instead of the then accepted value of 128. Hence ensued a vigorous study of tellurium, its purity, purification and atomic weight determination. Efforts were made in abundance to separate therefrom some constituent of higher atomic weight which would have a position below tellurium in the 6th group.

All these efforts were fruitless. A multiplicity of methods of purification all failed to yield a tellurium of atomic weight lower than that of iodine. The exception did not nullify the periodic law. The wonderful truth and value of the periodic relation were abundantly evident. As a consequence, and until the reason for the anomaly should reveal itself, tellurium and iodine were assigned to those group positions to which their properties, chemical and physical, indicated that they belonged, order of atomic weights notwithstanding.

Cobalt (58.97) and nickel (58.68) were similarly misplaced on the basis of order of atomic weights. The sequence from the standpoint of properties of the first three transitional elements is most certainly iron, cobalt, nickel, whereas the order of atomic weights is iron, nickel, cobalt. Again, the presence of another element, 'gnomium,' was suspected. Again, intensive and painstaking labors failed to reveal the element or reverse the order of atomic weights. Cobalt and nickel likewise remained anomalous.

One other pair of misfits arose with the discovery of the rare gases by Ramsay. Argon of atomic weight 39.88, an obvious member of Group O, was found to have an atomic weight greater than that of potassium, 39.10, again obviously a member of Group I. In view of these anomalies in the face of such overwhelming evidences of the approximate truth of the law in the majority of its details it is little wonder that Ramsay asked "Why this incomplete concordance?" The answer has emerged and in the unfolding of the mystery the student of chemical philosophy has much to learn. He will find an answer to the query of Ramsay. The incomplete concordance is evidence of the limitations to which many laws are subject, is evidence that the laws in question are but *approximations* to the fundamental law. The incomplete concordance is evidence of incomplete truth. The realization of this will be valuable, for it will give to authentic exceptions to general laws a vital importance in the search for truth. Science is full of illustrations of this fact. The exceptions to the Law of Dulong and Petit were an index of the approximate truth only of the law. It will be shown later that they constituted a sign post to a more fundamental law of the specific heats of elements of which Dulong and Petit's Law is but a limiting case. Ramsay himself found in the anomalous density of nitrogen from air and from nitrogen compounds as determined by Lord Rayleigh the sign post to a whole group of chemical elements at that time unknown. The anomalies in the periodic law were the arrows pointing to the necessity of obtaining yet more fundamental truths concerning the nature, the architecture and the periodic relationships of elementary matter. As the science progressed new sign posts appeared. The allocation of the rare earths to positions in the periodic table was a problem in itself of great complexity. The discovery of the radio-elements multiplied the difficulties of allocation. These difficulties gave to other less pronounced difficulties an added significance. Thus, for example, the problem of the odd and even series recurs. Copper, silver and gold are distinct variants from the alkali elements. Gold chloride, $AuCl_3$, seems out of place in the compounds of the elements of Group I. Lead resembles thallium, mercury is similar to

copper. Magnesium behaves like manganese in some of its compounds. In the ultimate solution, such problems will find their elucidation.

The Periodic Law and Electrochemistry: Faraday concluded that the laws of electrochemical action which he deduced were consonant with the facts of the atomic theory. Subsequent researches of Grove, Clausius, Hittorf, and Arrhenius established that, in conducting solutions, the elementary constituents were present, not as atoms, but as charged ions. It is of interest to examine the nature of these postulated ions in terms of the Mendeleeff classification. In a simple solution of an electrolyte, say of sodium chloride, the ionic theory postulated the presence of positively charged sodium ions and negatively charged chloride ions

$$NaCl + aq = Na^{+}_{aq} + Cl^{-}_{aq}.$$

With an electrolyte such as barium chloride the solution contained barium ions with a doubly positive charge and twice the number of singly charged negative ions

$$BaCl_2 + aq = Ba^{++}_{aq} + 2Cl^{-}_{aq}.$$

With sodium sulphide on the other hand the opposite distribution of charges was postulated

$$Na_2S + aq = 2Na^{+}_{aq} + S^{--}_{aq}.$$

Similarly, aluminium chloride dissociates thus:

$$AlCl_3 + aq = Al^{+++}_{aq} + 3Cl^{-}_{aq}.$$

In terms of electrochemical theory, therefore, the elements of Group I yield univalent positive ions, Group II divalent positive ions, Group III trivalent positive ions. Group VII contains the elements yielding univalent negative ions, Group VI elements yielding divalent ions, Group V the trivalent negative ions, though these are rare. On the left of Group IV are to be found the pronouncedly electro-positive elements, to the right the more pronouncedly electronegative compounds. These facts are of importance in the ensuing development of atomic structure. They provide a background from which to approach the newer ideas.

Atomic Structure: The atomic theory of Dalton provides, as has been shown, a satisfactory basis for the laws of chemical combination and the atomic weight provides a useful, if not completely satisfactory, basis for the classification of the elements. The concept of definite and indivisible atoms, of different weights, could not, however, be the ultimate solution of the problem of material structure. It provides no answers to a variety of problems. The difference in chemical properties between two atoms, say hydrogen and oxygen, can never be satisfyingly relegated to a simple difference in weight. Wherein does the difference in weight lie? What factors determine the weight difference? Furthermore, a number of physical and chemical properties of elementary substances cannot be explained upon any basis of weight variation of ultimate

indivisible particles. The varying valence of the different elements and also the varying valences of a single element remain entirely unexplained on the basis of the simple atomic theory. The spectral differences among the elements are likewise unexplainable. As has already been emphasized, the similarity and periodicity of properties, both physical and chemical, is the strongest possible evidence that like elements must possess similarities of architecture not envisaged by a theory of indivisible atoms. The inadequacies of the periodic system of classification are further sign posts indicating the need for further exploration of the composition of the individual atoms. Dalton had a glimpse from whence progress might come, for in his address to the Royal Society, upon receiving the Royal Medal he stated:

"The causes of chemical change are as yet unknown, and the laws by which they are governed; but, in their connexion with electrical and magnetic phenomena there is a gleam of light pointing to a new dawn in science."

The Electron: It is of interest to note that the development of the concept of atomic structure commenced when the concept of atomic electricity received its first quantitative study. Faraday's experiments on the conduction of salt solutions are the first experiments indicative of discrete units of electricity. G. Johnstone Stoney in an address before the British Association in 1874, published in 1881,[1] definitely emphasizes this fact.

"Nature presents us with a single definite quantity of electricity which is independent of the particular bodies acted on. To make this clear, I shall express Faraday's Law in the following terms, which, as I shall show, will give it precision, viz.: For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte which is the same in all cases."

Helmholtz in the Faraday lecture at the Royal Institution in 1881 emphasized the same point of view:

"Now the most startling result of Faraday's Law is perhaps this, if we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions which behave like atoms of electricity."

G. Johnstone Stoney, 1891, gave to the 'natural unit of electricity,' thus defined in reference to Faraday's Law, the name 'electron.' Faraday's Law, however, was not sufficient to establish the atomistic concept of electricity. It applied only to solutions of electrolytes. Metallic conduction was still discussed in terms of 'ether strains' and 'continuous homogeneous fluids.' The proof of atomic electricity did not come until the mechanism of gaseous conduction had been studied and the properties of gases acted upon by X-radiation and radioactive materials had become familiar.

The experiments of J. J. Thomson and his collaborators at the Cavendish Laboratory, Cambridge, England, supplied the original information in this field. Gases treated with X-rays were found to be conducting. The conductivity thus induced in a gas was caused by an agency which could be removed

[1] *Phil. Mag.*, (5) 11, 384 (1881).

by filtration through glass wool, by passage of the gas through metal tubes or between plates maintained at a sufficiently large potential difference. The conductivity was therefore due to electrically charged particles. More detailed knowledge of the nature of the charged particles was obtained by a study of the conduction of electricity through gases at low partial pressures. When currents at high potentials are discharged through gases at pressures of about 0.01 mm. or lower, charged particles or corpuscles are shot off from the cathode. These particles, first investigated by Sir Wm. Crookes, and called by him the 'fourth state of matter,' have properties the study of which led eventually to an appreciation of their importance in atomic structure. The cathode particles were shown to have the following properties:

(1) They travel in straight lines normal to the cathode and cast shadows of opaque objects placed in their path.

(2) They are capable of producing mechanical motion.

(3) They produce phosphorescence in many objects exposed to their action, e.g., blue phosphorescence in lead glasses.

(4) They produce a rise in temperature in objects which they strike.

(5) They may be deflected, by electromagnetic and electrostatic fields, from their normal rectilinear paths.

(6) The charge carried by the particles is negative since they electrify negatively insulated metallic electrodes upon which they fall.

(7) They may penetrate thin sheets of metal, the stopping power of the metal varying directly with the thickness of the metal and with its density.

(8) They act as nuclei for the condensation of supersaturated vapors. The fogs thus formed are useful as a means of rendering the particles visible.

(9) The particles were identical in nature and in the ratio of charge carried to mass of the particles, *irrespective of the nature of the residual gas in the discharge tube.* This represented the first definite indication that the *cathode particles were a common constituent of all atoms.*

The Velocity of the Cathode Particle: The velocity of the particle can be determined by measuring the displacement effected by known electrostatic and electromagnetic fields on a fine pencil of cathode particles. Such a pencil of particles impinging on a phosphorescent screen may be located by the phosphorescent spot produced. If a strong magnetic field H be applied to such a pencil of rays they will be deflected from their rectilinear path. The force exerted by the field H on a particle carrying a charge e, moving with a velocity v, will be Hev. At equilibrium, this force will be equal to the centrifugal force of the moving particle acting outwards along its radius of curvature, r. Therefore, if the mass of the particle be m, the following relation holds

$$Hev = \frac{mv^2}{r}.$$

Since H and r are both measurable it follows that the ratio $mv/e = Hr$ can be determined. Now, by superposing on the pencil of cathode particles thus magnetically deflected a suitable electrostatic field X, the pencil may be restored to its original rectilinear path. In such case, by equating the electrostatic and electromagnetic forces involved, there follows

$$Xe = Hev$$

whence v may be determined from the known values of X and H. Hence also the ratio e/m may be obtained.

By removing the electromagnetic field, a further check upon the value of e/m may be obtained. The electrostatic field deflects the corpuscles from their normal rectilinear path. The downward acceleration $\left(= \frac{\text{force}}{\text{mass}}\right)$ produced by the action of the electrostatic field is Xe/m. The distance through which the particle will fall in time t is

$$d = \frac{1}{2}\frac{Xet^2}{m}.$$

Now $t = l/v$ where l is the distance travelled by a particle of velocity v. Hence, the vertical displacement, d, as revealed by the change in position of the phosphorescent spot is given by

$$d = \frac{1}{2}\frac{Xe}{m}\frac{l^2}{v^2}.$$

Since d and l may be measured, X is known and v deduced as indicated above, it is possible to calculate e/m from the equation

$$\frac{e}{m} = \frac{2dv^2}{X\,l^2}.$$

By these methods Thomson was able to show that the ratio e/m was constant for all cathode rays, irrespective of the nature of the electrodes or the nature of the residual gas in the discharge tube for all velocities of travel not approaching the velocity of light. The average value of v was found to be 2.8×10^9 cm. per second. The value of e/m in such discharge tubes was approximately 1.79×10^7 electromagnetic units. This may be compared with the ratio of e/m for a hydrogen ion. It was known that the charge carried by such an ion is 4.77×10^{-10} electrostatic units. The mass of a hydrogen ion is 1.64×10^{-24} grams. Hence in electromagnetic units, the charge e/m for a hydrogen ion is

$$\frac{4.77 \times 10^{-10}}{1.64 \times 10^{-24} \times 3 \times 10^{10}} = 0.97 \times 10^4 \text{ electromagnetic units.}$$

For the cathode particle therefore the ratio e/m is approximately

$$\frac{1.79 \times 10^7}{0.97 \times 10^4} = 1845 \text{ times}$$

greater than that for the hydrogen ion. It is apparent that one of several factors may account for this: (1) either the charge on the particle is some 1845 times greater than that on the hydrogen ion, the masses being identical, or (2) the mass of the particle may be 1/1845 of the mass of the hydrogen ion and the

charges identical or (3) the cathode particle may differ in both charge and mass from that of the hydrogen ion. It will now be shown that the charge of the cathode particle is identical with that of the hydrogen ion and that, therefore, the mass of the cathode particle is approximately 1/1845 of the hydrogen ion.

The Charge Carried by a Cathode Particle: The earliest efforts to determine e were made by Townsend,[1] J. J. Thomson[2] and H. A. Wilson.[3] Townsend produced his charged particles by electrolysis of solutions at high current densities. The gases thus evolved contain a small fraction of the molecules in the charged condition. When these charged gases were bubbled through water they formed a cloud or fog which could be discharged by bubbling through concentrated sulphuric acid. The removal of the moisture in this manner did not entirely destroy the charge on the gas. Repetition of the procedure would give new clouds. Townsend assumed that the number of ions was the same as the number of fog particles. He determined the total electric charge per cubic centimeter carried by the gas. He determined the total weight of the cloud by absorbing the water in sulphuric acid. He found the average weight of the water droplets by observing their rate of fall under gravity, computing their mean radius by the application of Stokes' law,

$$v = \frac{2}{9}\frac{gr^2d}{\eta},$$

where v is the velocity of fall of a drop of water of radius r and density d, falling through a gas of viscosity η, under the acceleration of gravity g. From these data Townsend computed the number of droplets, assumed equal to the number of ions, and hence the average charge carried by each ion. His mean determinations gave $e = 3 \times 10^{-10}$ electrostatic units.

Thomson's method was similar to Townsend's but utilized the observation of C. T. R. Wilson that the sudden expansion and consequent cooling of the air in the ionization vessel gave a convenient method of producing the cloud formation. The ionization was produced by means of X-rays which give rise to negative particles or ions and positive particles which are the residues from which the corpuscles have been removed. By adjusting the degree of supersaturation, condensation may be confined to the negative particles as was demonstrated by H. A. Wilson. Thomson obtained his measurement of total charge carried by the cloud by determination of the current carried by the cloud under the influence of a weak electromotive force. Thomson weighed the cloud produced and utilized Stokes' Law as in Townsend's work. As a final value for e Thomson gave $e = 6.5 \times 10^{-10}$ (1898). Later work [4] with radium as the source of ionization gave him the result 3.4×10^{-10}.

Thomson's mode of experimentation was modified by H. A. Wilson who studied the rate of fall of the cloud under gravity alone and also under the

[1] *Proc. Camb. Philos. Soc.*, 9, 244 (1897).
[2] *Phil. Mag.*, 46, 528 (1898).
[3] *Phil. Mag.*, 5, 429 (1903).
[4] *Phil. Mag.*, (6) 5, 354 (1903).

combined action of gravity and an electrostatic field. The ratio of the velocities, v_1 and v_2, under gravity alone and with the combined action of gravity and an electrostatic field X is given by the equation

$$\frac{v_1}{v_2} = \frac{mg}{mg + Xe}.$$

Combining this with Stokes' Law for v_1

$$v_1 = \frac{2}{9}\frac{gr^2d}{\eta}$$

and eliminating m by the expression $m = 4/3\ \pi r^3 d$, Wilson obtained the expression

$$e = \left\{ \frac{4}{3}\pi \left(\frac{9\eta}{2g} \right)^{3/2} \right\} \frac{g}{X} \frac{(v_2 - v_1)}{d^{1/2}} v_1^{1/2}.$$

This yielded for e a mean value of 3.1×10^{-10} electrostatic units. The deviations were considerable, the extreme values being 2.0×10^{-10} and 4.4×10^{-10} E.S.U. Wilson's method eliminated the assumption as to the equality of the number of droplets and the number of ions. It involved the assumption, however, that successive cloud formations gave equally sized droplets, an assumption which later work by Millikan could not be found to sustain with any certainty.

Millikan's first work with Begeman was essentially a repetition of the H. A. Wilson method using radium as the ionizing agent and a 4000 volt storage battery to charge the plates. The results were more consistent than Wilson's and gave as the mean of the observations, varying between 3.66×10^{-10} and 4.37×10^{-10}, a value $e = 4.06 \times 10^{-10}$ E.S.U.[1]

Millikan's 'balanced-drop' method:[2] This represents a distinct advance on the H. A. Wilson method. To eliminate errors due to evaporation, Millikan planned to use a sufficiently strong field, to balance exactly the force of gravity on the droplets and thus maintain the top surface of the cloud stationary. Without attaining this object, he succeeded in the more important task of studying the behavior of *individual droplets.* He found they could be held suspended in the field from 30 to 60 seconds; that they carried multiple charges varying between $2e$ and $6e$. These charges were all exact multiples and therefore reveal positively the unitary nature of electricity. The ionized cloud after formation between the plates was subjected to a given potential gradient. This removes all of the cloud particles with the exception of those which have the right ratio of charge to mass to be held in suspension in the field. Observations on these droplets were made with a telescope in the eyepiece of which three equally spaced cross hairs were placed. A small section of the space between the plates was illuminated by a narrow beam of light suitably freed from its heat rays by three water cells in series. The cross hairs were set

[1] *Phys. Rev.*, **26**, 198 (1908).
[2] *Phil. Mag.*, **19**, 209 (1910).

near the lower plate and as soon as a stationary drop was found somewhere above the upper cross hair it was watched for a few seconds to make sure that it was not moving. The field was then thrown off and the plates shortcircuited. The drop was then timed in its fall by means of a stop-watch as it passed across the three cross hairs. It will be seen that this method furnishes a check upon evaporation; for, if the drop is stationary at first it is not evaporating sufficiently to influence the readings; if it begins to evaporate before the readings are completed, the time required to pass through the second space should be greater than that required to pass through the first space. In general this was not the case.

The preceding equation of the Wilson method, applied to the balanced droplet, assumes the form

$$e = 3.422 \times 10^{-9} \frac{g}{X} (v_1)^{3/2}.$$

In this case, the electrostatic field X is so opposed to gravity that $v_2 = 0$. The constant 3.422×10^{-10} was chosen by Millikan as most accurately representing the terms in the Wilson equation involving the viscosity of the medium and the density of the droplets. From these determinations, Millikan deduced the value $e = 4.65 \times 10^{-10}$ E.S.U., with extreme values of 4.87×10^{-10} and 4.56×10^{-10} E.S.U.

Millikan's Oil Drop Method:[2] This later method of Millikan's represents the most accurate method of determination of the unitary quantity of electricity disclosed by the previously mentioned investigation. A diagram of this apparatus is appended. The droplets investigated were introduced into the

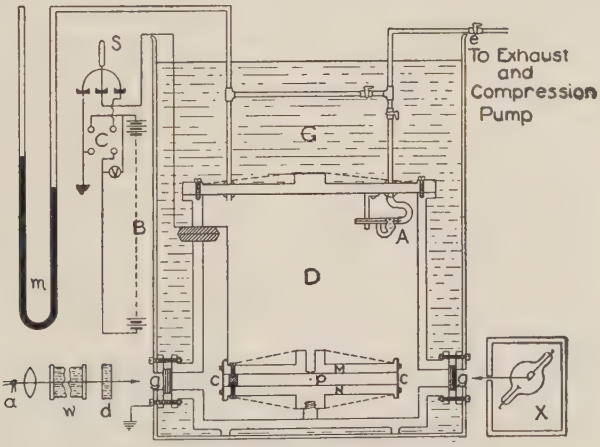

FIG. 1. Millikan's Oil Drop Apparatus

chamber D by means of the atomizer A in the form of a finely divided spray. Eventually one of these droplets finds its way through the aperture, p, into

[2] *Phys. Rev.*, 2, 143 (1913).

the space between the condenser plates, M and N. The hole p is then closed and the air between the plates ionized by a source of X-rays, X. Illumination is secured from the arc lamp, a, the heat rays being removed in filters w and d. The motion of the illuminated droplet is observed through a microscope fitted with an engraved scale. By collision with ions of the air the droplet acquires an electric charge, and then moves between plates M and N in a direction governed by the sign of the acquired charge and with a speed indicative of the sign of the charge carried. By reversal of the sign of the charge on M and N the direction of motion of the droplet can be reversed. In this way the droplet could be kept travelling back and forth between the plates. As a mean of 17 determinations of the times which the droplet required to fall between two fixed cross hairs in the observing telescope, whose distance apart corresponded to a distance of fall of 0.5222 cm., a value of 13.595 seconds with a maximum deviation of $\pm$ 0.2 sec. was obtained. When rising under the influence of an electric field produced by applying a potential difference of 5051 volts, the successive times required varied in the following way: 12.5, 12.4, 21.8, 34.8, 84.5, 84.5, 85.5, 34.6, 34.8, 16.0, 34.8, 34.6, 21.9 seconds. It will be seen that, after the second trip up, the time changed from 12.4 to 21.8, indicating, since in this case the drop was positive, that a negative ion had been caught from the air. On the next trip another negative ion had been caught. The next time, 84.5, indicates the capture of still another negative ion. From the equation

$$\frac{v_1}{v_2} = \frac{m_d g}{Xe - m_d g} \qquad \text{or} \qquad e = \frac{m_d g}{X v_1}(v_1 + v_2),$$

where m_d is the mass of the droplet, it follows that the change in velocity produced by the acquiring of an extra charge can be given by eliminating m_d and solving the equations thus:

$$(a) \quad t = 34.8 \text{ secs. against gravity } v_1 + v_2 = \left(\frac{0.5222}{13.595} + \frac{0.5222}{34.8}\right);$$

$$(b) \quad t = 84.5 \text{ secs. against gravity } v_1 + v_2 = \left(\frac{0.5222}{13.595} + \frac{0.5222}{84.5}\right).$$

The time difference between (a) and (b) is

$$0.5222\left(\frac{1}{34.8} - \frac{1}{84.5}\right) = 0.00891 \text{ cm. per second.}$$

In this manner it was shown that successive captures of an ion effected changes in the velocity of rise against gravity respectively equal to 0.008912, 0.008911, 0.008903, 0.008883 and 0.008931 cm. per second, all of which are within 1/5th of 1 per cent of the mean value of 0.00891 cm. per second. This therefore represents the change in the sum of the speeds v_1 and v_2 caused by the capture of one ion. Relationships of this sort were found to hold absolutely without exception, no matter in what gas the droplets had been suspended or what sort

of droplets were used upon which to catch the ions. Experiments were conducted over five or six hours, hundreds of ions per droplet were caught and recorded by the change of speed. Here then is direct proof that the electrical charges found on ions all have exactly the same value or else small exact multiples of that value. This is the most conclusive proof of the 'atomic' structure of electricity.

From the preceding equation, with the data obtained in this study of the behavior of the oil droplets, accurate values for the ratio e/m_d could be deduced. To obtain the magnitude of the unit charge e it was necessary however to determine the mass of the droplet. For this purpose Stokes' Law could be employed to determine the radius and therefore the volume and mass of the droplet. To attain in these calculations the same high degree of precision which was obtained in the velocity determinations just recorded, Millikan found it necessary to make an investigation into the limitations of Stokes' Law with variation in the medium and with variation in the droplet size. On completion of this study, which revealed the necessity of correcting Stokes' Law for inhomogeneities in the medium—a correction which was finally made as an empirical function of the ratio of the mean free path of the gas molecules of the medium, l, to the radius of the droplet r— Millikan derived a corrected form of the Stokes' equation from which the radius of the droplet was determined,

$$v_1 = \frac{2}{9}\frac{gr^2}{\eta}(d_d - d_m)\left(1 + A\frac{l}{r}\right)$$

in which d_d is the density of the drop, d_m that of the medium, A an empirical constant, the other terms having the same significance as given previously. In this manner, the magnitude of e was finally obtained with a degree of precision embodied in the following expression:

$$e = (4.774 \pm 0.005) \times 10^{-10}.$$

The Avogadro Constant: The determination of e with the degree of precision herein indicated gives at once a most valuable method of evaluating the Avogadro constant, the number of molecules in one gram molecule of any gas under standard conditions of temperature and pressure. This is readily achieved by combining this value of e with that obtained in electrochemical work for the value of the Faraday, the quantity of electricity necessary to liberate one gram ion of a monovalent element in electrolysis. By international agreement it has been decided that the atomic weight of silver is 107.88 and the unit of electricity expressed in electromagnetic units has been defined as the amount of electricity which will deposit from a silver solution 0.1118 gram of silver. The value of the Faraday is therefore

$$\frac{107.88}{0.1118} = 9650 \text{ electro-magnetic units}$$

or, in electrostatic units, $9650 \times 2.9990 \times 10^{10}$ E.S.U. This quantity is equal

to the elementary charge, e, multiplied by the Avogadro number N. Hence,

$$4.774 \times 10^{-10}N = 9650 \times 2.9990 \times 10^{10}$$

or

$$N = 6.062 \times 10^{23}$$

the precision of which is given by the expression

$$N = (6.062 \pm 0.006) \times 10^{23}.$$

The Mass of the Hydrogen Molecule: Given N, the Avogadro number, the mass of the hydrogen molecule is obtained from the molecular weight of hydrogen by simple division. The mass of the individual molecule becomes

$$\frac{2.016}{6.062 \times 10^{23}} = (3.324 \pm 0.004)10^{-24} \text{ gram.}$$

The Mass of the Electron: Millikan's work established the identity of the charges on an electron and a monovalent ion. It is evident therefore that the masses of the hydrogen atom and the electron must be in the same ratio as the respective ratios e/m and E_{H^+}/M_{H^+} bear to one another. As has already been shown, these ratios are in the ratio of 1 to 1845. Hence the mass of the electron becomes

$$\frac{1.662 \times 10^{-24}}{1845} = 9.0 \times 10^{-28} \text{ grams.}$$

It should be observed that this mass applies only to such electrons as are moving slowly relative to the velocity of light, which is true of electrons produced in the experiments on the discharge of electricity through gases. As the velocity increases, the mass becomes correspondingly greater; when the corpuscle attains the velocity of light its mass, theoretically, is infinite. Swiftly moving particles, products of radioactive decay, are known with over 90 per cent of the velocity of light, and the variation of the mass of the negative electron with speed agrees accurately with the rate of variation computed on the assumption that this mass is all of electromagnetic origin.

Mechanism of Ionization of Gases: The early work of Townsend, previously discussed, together with his measurements on the diffusion coefficients and the mobilities of the gas ions produced in his experiments, led him to the conclusion that both positive and negative ions carry unit charge. Some later data of Townsend suggested that the positive ions were possibly doubly charged.

Experiments of Franck and Westphal,[1] analogous to those of Townsend, led to the conclusion that all the negative and the majority of the positive ions carry unit charge. A small fraction, about 9 per cent, of the positive ions appeared to be doubly charged when X-radiation was the ionizing medium. With α, β and γ rays from radioactive sources they found no evidence of doubly charged ions.

[1] *Verh. deutsch. phys. Ges.*, March, 1909.

Millikan and his co-workers have repeated the studies of the mechanism of ionization, employing the technique developed in the work detailed in the preceding sections. The conclusions to which this study led may be summarized in the following way:[1]

(1) The action of ionization by β-rays seems to consist in the release, without any appreciable energy, of one single electron from an occasional molecule through which the β-ray passes. The faster the β-ray the less frequently does it ionize.

(2) The act of ionization by X-rays or light seems to consist in the hurling out, with an energy that may be very large, but which depends on the frequency of the ether wave, of one single electron from an occasional molecule over which this wave passes.

(3) The act of ionization by rapidly moving α-particles consists in the shaking loose of one single electron from the atom through which it passes; a slow moving positive ray appears in some cases to be able to detach several electrons from a single atom.

This last conclusion is abundantly verified by the recent studies of J. J. Thomson and of Aston on the positive rays. Mass-spectrographic data reveal abundant evidence of multiply-charged atomic masses.

Ionization may result from chemical action as well as by means of the physical agencies already considered. There is a growing body of evidence indicating the presence of ions in reacting gaseous systems, persistent even when excessive precautions to exclude ion-producing mechanisms of a physical nature are excluded. Pinkus has reported [2] ionization in certain gas reactions. Recent work by Brewer and Daniels[3] demonstrates ionization in the interaction of nitric oxide and oxygen, a reaction for which Pinkus previously obtained negative results. The later work indicates definite though small ionization, of the order of 10^{-14} amperes for the oxidation of 50 cc. of nitric oxide per minute reacting in a field of 450 volts per cm. It should be observed that such ionization may be incident to, but not essential in, chemical reactions.

This evidence, therefore, points undoubtedly to an atomic architecture in which the neutral atom is built up of negative electrons and positive rests or nuclei.

Size of the Electron: Assuming that the mass of the electron is entirely of electromagnetic origin, the size of the electron can be calculated from the equation

$$m = \frac{2}{3}\frac{e^2}{a},$$

which relationship connects the mass, m, with the charge e carried by a sphere of radius a. Solving this equation for a with the accepted values for m and e, the radius of the sphere over which the mass must be distributed proves to be

$$a = 2 \times 10^{-13} \text{ cm.}$$

[1] Millikan, The Electron, pp. 140, 141.
[2] *J. Chem. Phys.*, 18, 366, 412 (1920).
[3] *Trans. Am. Electrochem. Soc.*, Oct. 1923.

It is of importance to note that this is an entirely lower order of magnitude than the atomic radius which approximates to 10^{-8} cm. (See Chapters III and V.)

Size of the Positive Nucleus: There is no direct experimental justification for the assumption that the mass of the nucleus is entirely of electromagnetic origin. If this were so however, it is evident that, since the mass, m, of the hydrogen nucleus is 1845 times as large as that of the electron, the radius a of a hydrogen nucleus, with the mass assumed to be of electromagnetic origin, would be 1/1845 that of the electron or, approximately, 1×10^{-16} cm.

From these considerations, it is evident that the hydrogen atom would consist of a minute speck of positive electricity relatively remotely distant from a negative electron, 1845 times larger in radius, these two charged specks occupying positions within the atom the linear dimensions of which would be respectively about 1×10^{-8} and 2×10^{-5} of that of the atom. The hydrogen atom therefore could literally be said to be two tiny specks of charge in almost an infinity of space.

Proof of the minuteness of the atomic nucleus is obtainable by a study of the tracks of α-particles and β-particles through gases. Photographs of such tracks are obtainable, for the gas through which the particles travel is ionized and the ions may be rendered visible by the condensation of water vapor upon them.[1] Study of photographs so obtained shows that a β-particle may pass through as many as 10,000 atoms before it comes near enough to an electronic constituent of any of the atoms to detach it from its system and form an ion, a circumstance which indicates the relative freedom of the atomic space from such electronic constituents. Furthermore, α particles, owing to their great mass relative to the electron (approximately 7000 : 1), are uninfluenced by the electrons with which they come in contact. They may however be stopped or deflected by the more massive positive nuclei of the atoms through which they pass. Photographs reveal, however, that, on an average, an α-particle goes through 200,000 atoms without approaching near enough to the nucleus to suffer appreciable deflection. The conclusion seems inescapable therefore that the positive nucleus is also but a minute fraction of the total atomic volume.

The Nuclear Atom: The facts thus ascertained with regard to the components of the atom have led Rutherford to the formulation of the nuclear atom theory. According to Rutherford an atom consists of a heavy minute positively charged nucleus surrounded by electrons probably situated to the nucleus somewhat as the planets are situated to the sun. The number of electrons outside the nucleus is equal to the net positive charge on the nucleus.

Rutherford,[2] Geiger and Marsden[3] by studies of the deflections suffered by α-particles in passing through various metal foils were able thence to calculate the number of free positive charges on the metal atoms through which the

[1] C. T. R. Wilson, *Proc. Camb. Phil. Soc.*, 9, 333 (1897); *Phil. Mag.*, 7, 681 (1904).
[2] *Phil. Mag.*, 21, 669 (1911).
[3] *Phil Mag.*, 25, 604 (1913).

α-particles passed. They concluded that the number of free positive charges was approximately equal to half the atomic weight. This conclusion was in striking agreement with earlier work by Barkla[1] on the scattering of X-rays. This work indicated that, in each atom, the number of scattering centers, namely, the electrons, was approximately equal to one half the atomic weight. Evidence, therefore, was available with both positive and negatively charged portions of the atom as to this relationship between atomic weight and elcctrical charge.

The Atomic Number: The actual count, with precision, of the extra-nuclear electrons in elementary substances was accomplished by Moseley, 1914.[2] The suggestion of Laue, 1912, that the regular spacing of atoms in a crystal could be utilized, on the principle of a grating, for the analysis of short wave-length ether waves, had been translated into actual practice by the Braggs,[3] an X-ray spectrometer devised and the wave lengths of various X-rays determined. Moseley, in 1914, utilizing a wide variety of elements as targets in the X-ray bulb, found that, in addition to general X-radiation which all emitted, each element emitted X-radiations characteristic of the given element. Moseley showed that the square root of the frequency (inverse wave length) of a given series of the characteristic X-ray spectra of the elements constituted an an arithmetical progression; the order of increasing frequency was that of the elements arranged in the order of their atomic weights with conspicuous and significant exceptions. A missing element in the periodic order gave a missing step in the increment of the square root of the frequency. In the whole series of elements ranging from hydrogen = 1 to uranium = 92, six gaps were found at the time of Moseley's discovery, indicating that, at this date, six elements below uranium were still unknown. Of these six, the existence of four has, in the meantime, been indicated. In 1923 Hevesy and Coster discovered Hafnium, No. 72.[4] In 1925 Noddack, Berg and Tacke announced the discovery of Masurium, No. 43, and Rhenium, No. 75, of which only the latter has since been intensively studied.[5] In 1926 Hopkins indicated the presence of Illinium, No. 61, in association with other rare-earth elements.[6] All these four elements were identified by X-ray spectrographic methods. The elements still missing are No. 85, in the halogen group and No. 87, the last member of the alkali group. Since the X-ray frequencies involved in Moseley's investigations are probably due to vibrations arising from electrons proximate to the nucleus, the additivity of the square-root of the frequency, observed by Moseley, indicates or suggests that the charge on the nucleus in a given element differs from that of the nucleus of the preceding element in the periodic classification by a constant and definite charge.

[1] *Phil. Mag.*, **21**, 648 (1911).

[2] *Phil. Mag.*, **26**, 1024 (1913); **27**, 703 (1914).

[3] X-rays and Crystal Structure, 1915.

[4] *Nature*, **111**, 79, 182, 252 (1923); Cf. *Chem. Rev.*, **2**, 1 (1925).

[5] Noddack and Berg, *Sitz. ber. Preuss. Akad.*, June 1925; *Naturwiss.*, **13**, 567 (1925); *Z. physik Chem.*, **125**, 264 (1927).

[6] Harris and Hopkins, *J. Am. Chem. Soc.*, **48**, 1585 (1926).

Radioactive Disintegration and Atomic Structure: Confirmation of this conclusion from Moseley's work came from study of radioactive decay in its relation to periodic classification. As knowledge of the properties of the elements formed in the successive stages of radioactive decay became more complete, it emerged that the loss of α-particles and β-particles by a radioactive element corresponded to a definite shift of the group classification of the elements produced in the process of decay. The loss of an α-particle in *every* case produced a shift, two groups to the left in the periodic table. Thus Radium (Group II) loses an α-particle to give Radon (Ra. Emanation) Group 0. Similarly loss of a β-particle gives rise to a shift of one group to the right in the periodic table. The change of Radium B, Group IV to Radium C, Group V is one illustration of such change (see, in addition, Chapter XXI). This important generalization is shared by several investigators: notably Soddy,[1] Fleck,[2] Russell[3] and Fajans.[4] Now, since the α-particle is a helium nucleus carrying a double positive charge and since the β-particle is none other than an electron, and since, moreover, these particles are certainly ejected from the nucleus, it follows that the difference between the nuclei of successive atoms in neighboring groups of the periodic table consists in the extra unit of positive charge which the heavier nucleus possesses. The atom itself being electrically neutral, it therefore follows that the extra-nuclear electrons must increase by one as the atomic table is ascended. The progressive variation in the square root of the frequency of the characteristic X-radiation as discovered by Moseley is therefore paralleled by a progressive increase of net positive nuclear charge and of extra-nuclear electrons.

Upon this basis, the assumption is natural that the hydrogen atom consists of a proton or unit positive charge of mass = 1 and a negative electron. The helium nucleus on this basis will be composed of four protons with two nuclear electrons giving the nucleus a net positive charge of two, requiring two extra-nuclear electrons to complete the neutral atom. Similarly, lithium nucleus will have net positive charge of 3 with three external electrons, beryllium will have 4 such, boron 5, carbon 6, nitrogen 7, oxygen 8, fluorine 9 and so on. To the net nuclear charge or, what is the same thing, to the number of extra-nuclear electrons as revealed by the Moseley investigations, the term atomic number has been assigned. In the periodic classification given in a preceding section the atomic numbers of the elements have been given in addition to the atomic weights.

The Atomic Number and Defects in the Periodic Table: It was shown that on the basis of weight classification certain definite transpositions of the elements would occur which would not be in harmony with the periodicity of properties shown by the bulk of the elements when arranged on a weight basis. The transposition of argon and potassium, of tellurium and iodine and of cobalt and nickel was noted. When studied by the Moseley method, the

[1] Chemistry of the Radio Elements, Part II, p. 2, 1914; *Chem. News*, **107**, 97 (1913).
[2] *J. Chem. Soc.*, **103**, 381, 1052 (1913).
[3] *Chem. News*, **107**, 49 (1913).
[4] *Physikal. Z.*, **14**, 49, 131, 136 (1913).

order of the square root of the characteristic frequencies of these elements was such as would be anticipated on the basis of properties and not that obtained on the basis of atomic weight. Argon therefore has an atomic number of 18, potassium 19, cobalt 27, nickel 28, tellurium 52, iodine 53. The answer to the query of Ramsay as to the lack of complete concordance in the periodic classification was evident and revolutionary. The atomic weight is not the fundamental factor in atomic behavior. The properties of the elements are a function of their atomic architecture. Atomic weight is a secondary factor

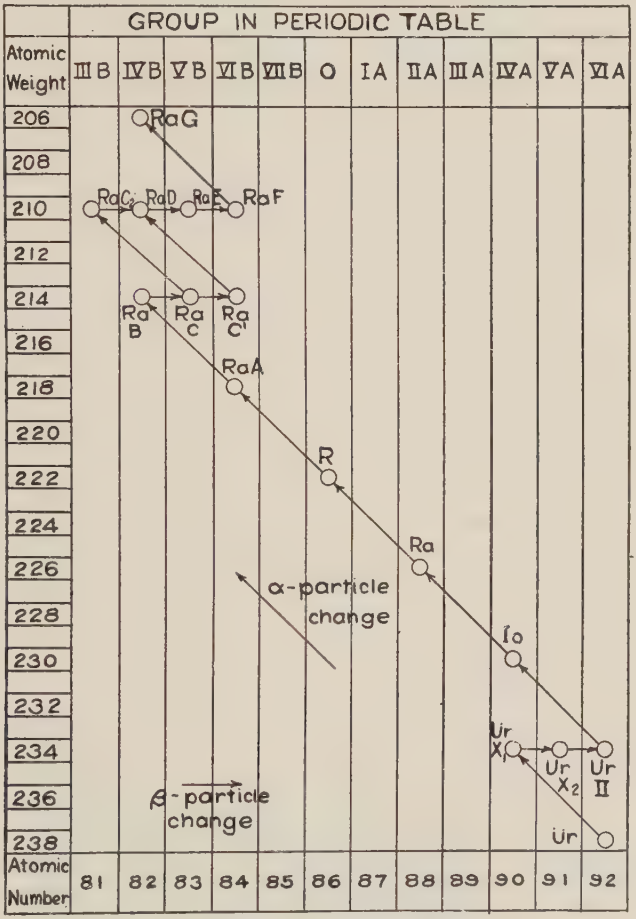

FIG. 2. Radium Disintegration Series

useful as a guide in the great majority of cases but at fault in the cases just mentioned and certain others now to be discussed.

Isotopes: The existence of elements differing in mass yet identical in chemical properties was made familiar by the study of radioactive decay. It gradually

emerged that the end product in the decay of radium was Radium G, radio-lead, identical in chemical properties with that of ordinary lead. Moreover, as the change in group classification brought about by loss of α- and β-particles became understood, it was further evident that Radium B, Radium D and Radium G were all members of Group IV in the periodic classification. This is evident from the accompanying chart. Furthermore, since loss of an α-particle (helium nucleus) results in a diminution in the atomic weight by four units, while the β-particle change is without influence on the weight, it is evident that, by calculation of the α-particles lost in the successive changes, the atomic weights of successive products could be deduced from that of radium. Assuming an atomic weight of 226 for radium, that of Ra B becomes 214 (3 α-particles lost), that of Ra D becomes 210 (4 α-particles lost), and Ra G becomes 206 (5 α-particles lost). All these elements have properties identical with those of ordinary lead, whose atomic weight is 207.2, in all properties except those dependent upon mass. The masses differ as can be seen from the above examples by so much as eight units (206–214). The end-product of the thorium series of radioactive elements is likewise a member of Group IV analogous to lead with an atomic weight of 208.1. To such elements, identical in properties other than those dependent upon mass, the term *isotopes* was applied. The conclusions reached upon the basis of calculation from the atomic weight of lead and the α-particle loss have been abundantly confirmed by actual atomic weight determinations.[1] [2] [3]

The wide variety of elements produced in radioactive decay, their similarity of properties, in spite of wide differences in atomic weight, would have presented a problem of considerable complexity for periodic classification had not the Moseley discovery elucidated the true basis of classification and demonstrated the secondary importance of the weight relationship. All such isotopes while differing greatly in mass are identical in atomic number. Their net nuclear charges are identical. They have a common extra-nuclear electronic configuration. They differ only in the mass of the nucleus.

Non-Radioactive Isotopes: The existence of atoms of identical nuclear charge but differing masses, outside the range of radioactive materials, was demonstrated by the investigations of J. J. Thomson and of Aston on the properties of the positive rays from a discharge tube. In the earlier sections, a considerable discussion has been given of the electrons liberated from atoms by the action of various forms of energy. Little has been stated concerning the residues from such changes. Positive rays were discovered by Goldstein in 1886 in the discharge of electricity through gases at low pressure. Using a perforated cathode he showed that streamers of light were present behind the cathode perforations, and assumed that the light indicated the presence of rays travelling in the opposite direction from the cathode rays. From the manner of their production he termed them 'canal strahlen.' Wien[4] showed

[1] Richards and Lembert, *J. Am. Chem. Soc.*, **36**, 1329 (1914); **38**, 2613 (1916).
[2] Soddy, *J. Chem. Soc.*, **105**, 1402 (1914).
[3] Hönigschmidt, *Compt. rend.*, **158**, 1796 (1914).
[4] *Verh. d. Phys. Ges.*, **17**, 1898.

that they could be deflected by a magnetic field. The detailed investigation of their properties was undertaken by J. J. Thomson,[1] who gave to them the term Positive Rays since they were shown to carry a positive charge. The rays are produced by ionization of gases at low pressures in a strong electric field of the order of 30,000–50,000 volts. They are the residues from such ionization processes.

The method of measurement employed by Thomson to investigate the charge and mass of such rays is known as the 'Parabola' method. It consisted essentially in allowing the rays to pass through a very narrow tube and then in analyzing the fine beam so produced by electric and magnetic field. Under the combined influence of an electrostatic and an electromagnetic field a ray will be deflected from its normal path and will strike a receiving screen at a point x, y, where y/x is a measure of its velocity and y^2/x is a measure of e/m, the ratio of charge to mass. This follows from the application of simple dynamics to the separate actions of the electrostatic field X and the electromagnetic field H since

$$x = k\left(\frac{Xe}{mv^2}\right)$$

and

$$y = k'\left(\frac{He}{mv}\right)$$

in the manner previously demonstrated for the electron. The velocity v of the rays may vary however over a considerable range. Hence, for constant m but variable v, the locus of impact of the rays with the screen will be a parabola, pp' (Fig. 3). Rays of larger mass m' yield a similar parabola of smaller magnetic displacement qq'. The displacement of the parabolas along the magnetic axis OY at a given value along the electric field gives a measure of the relative masses since

$$\frac{m'}{m} = \frac{(pn)^2}{(qn)^2}.$$

With one known parabola, the mass of all other rays can be identified.

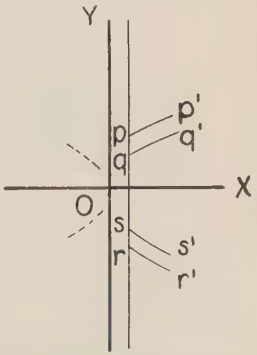

FIG. 3. J. J. Thomson's Parabola Method

The sharpness of the parabolas, obtained photographically in this way by using a photographic plate as receiving screen for the rays, established experimentally for the first time the fundamental assumption of the Daltonian atomic theory, that the atoms (in these experiments the positive rays) of the same element had the same mass.

A second method of positive ray analysis devised by Dempster[2] causes the

[1] Rays of Positive Electricity, 1913.

[2] *Phys. Rev.*, 11, 316 (1918).

charged particles to fall through a definite potential difference. A narrow bundle is separated out by a slit and is bent into a semicircle by a strong magnetic field; the rays then pass through a second slit and fall on a plate connected to an electrometer. The potential difference P, the magnetic field H and the radius of curvature r determine the ratio of the charge to the mass of the particle since

$$\frac{e}{m} = \frac{2P}{H^2r^2}.$$

This method is essentially that used by Classen[1] for the determination of e/m for electrons.

Aston improved the technique of positive ray analysis by the use of the mass-spectrograph illustrated in Fig. 4. Positive rays are sorted out into a thin ribbon by means of two parallel slits, S_1 and S_2, and are then spread into an electric spectrum by means of the charged plates P_1 and P_2. A portion of this spectrum deflected through an angle θ is selected by the diaphragm D and passed through the circular poles of a powerful electromagnet O, the field of which is such as to bend the rays back again through an angle ϕ, more than twice as great as θ. The result of this is that rays having a constant ratio m/e will converge to a focus F. If a photographic plate is placed at GF as indicated, a spectrum dependent on mass alone is obtained.

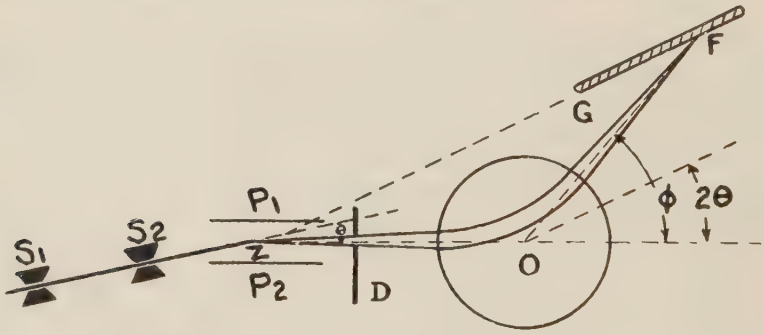

Fig. 4. Aston's Positive Ray Spectrograph

Aston[2] has been able, by successive improvements in his apparatus, to increase the accuracy of his measurements to as much as 1 part in 10,000. The early results showed that the light elements as well as the radio-elements may exist as isotopes and that the large deviations in the atomic weights of the elements from whole numbers were due to the presence of several isotopes of such masses and in such proportions as would yield the observed atomic weight. The results of such investigations (to the end of 1928) are shown in Table II.

Aston's discovery removes at once the only serious objection to the unitary

[1] Jahr. Hamburg. Wiss. Anst., Beiheft 1907.
[2] *Proc. Roy. Soc.*, 115A, 487 (1927).

TABLE II

ELEMENTS AND THEIR ISOTOPES

Element	Atomic Number	Atomic Weight	Minimum Number of Isotopes	Masses of Isotopes in Order of Intensity
H	1	1.008	1	1.008
He	2	3.99	1	4
Li	3	6.94	2	7, 6
Be	4	9.02	1	9
B	5	10.9	2	11, 10
C	6	12.00	1	12
N	7	14.008	1	14
O	8	16.000	1	16
F	9	19.00	1	19
Ne	10	20.2	2(3)	20, 22 (21)
Na	11	23.00	1	23
Mg	12	24.32	3	24, 25, 26
Al	13	26.97	1	27
Si	14	28.3	3	28, 29, 30
P	15	31.04	1	31
S	16	32.06	3	32, 34, 33
Cl	17	35.46	2	35, 37
A	18	39.88	2	40, 36
K	19	39.10	2	39, 41
Ca	20	40.07	2	40, 44
Sc	21	45.1	1	45
Ti	22	48.1	1(2)	48 (50)
V	23	51.0	1	51
Cr	24	52.0	1	52
Mn	25	54.93	1	55
Fe	26	55.84	2	56, 54
Co	27	58.97	1	59
Ni	28	58.68	2	58, 60
Cu	29	63.57	2	63, 65
Zn	30	65.37	7	64, 66, 68, 67, 65, 70
Ga	31	69.72	2	69, 71
Ge	32	72.5	8	74, 72, 70, 73, 75, 76, 71, 77
As	33	74.96	1	75
Se	34	79.2	6	80, 78, 76, 82, 77, 74
Br	35	79.92	2	79, 81
Kr	36	82.92	6	84, 86, 82, 83, 80
Rb	37	85.45	2	85, 87
Sr	38	87.63	2	88, 86
Y	39	88.9	1	89
Ag	47	107.88	2	107, 109
Sn	50	118.7	11	120, 118, 116, 124, 119, 117, 122, 121, 112, 114, 115
Sb	51	121.77	2	121, 123
I	53	126.92	1	127
Xe	54	130.2	9	129, 132, 131, 134, 136, 128, 130, 126, 124
Cs	55	132.81	1	133
Hg	80	200.6	7	202, 200, 199, 198, 201, 204, 196

theory of matter which, as has been previously recorded, lay in the deviations from whole numbers in the atomic weight tables. Thus, the hypothesis of Prout was hardly tenable while exact atomic weight determinations showed the atomic weight of chlorine to be 35.46. Aston's determinations reveal chlorine as a mixture of isotopic elements of masses 35 and 37 present in such a ratio as to give an atomic weight of the mixture equal to 35.46. Similarly with the other elements deviating from the whole number rule demanded on the basis of a unitary theory.

The discovery of isotopes explains also the remaining defect of the periodic classification, the inversion of argon and potassium, of tellurium and iodine and of cobalt and nickel in the arrangement of elements by weight. Thus, argon with an atomic weight 39.88 has isotopes of weight 40 and 36, the former in predominating amount. Potassium has two isotopes, 39 and 41, the former also largely predominating. In nuclear charge the argon isotopes are one less than those of potassium as the Moseley investigations reveal. The relative amounts of the two isotopes in each case determine the inversion of atomic weights. The same holds true for the heavier elements tellurium and iodine, cobalt and nickel.

Isotopes have identical nuclear charge but differ in mass. The isotopes of lithium have masses 6 and 7, the latter strongly predominant, since the atomic weight is 6.94. As the atomic number of lithium is three, it follows that the nucleus of Li^6 must be composed of 6 protons[1] with 3 electrons. That of Li^7 must contain 7 protons with 4 electrons. This gives each the net positive charge of 3 required. The planetary electrons are likewise 3 in number. The ordinary chemical properties of the element are determined by the planetary electrons, chemical change being confined to rearrangements and new combinations of such electronic systems in chemical compounds. The nuclei do not undergo any structural change in such chemical reactions. The processes of radioactive change were the first reactions involving nuclear change to be studied. It is from such studies that the architecture of the nucleus is now slowly being ascertained. Disintegration, which radioactive nuclei of themselves undergo, has now been achieved with the lighter elements, the nuclei of which can be disintegrated by collision with swift α-particles. Rutherford and Chadwick[2] have liberated swift hydrogen nuclei from the following elements, B(5), N(7), F(9), Ne(10), Na(11), Mg(12), Al(13), Si(14), P(15), S(16), Cl(17), Ar(18), K(19). They obtained negative results with a number of other elements notably carbon and oxygen. Kirsch and Petterson,[3] on the other hand, have obtained hydrogen nuclei from all the light elements with the exception of helium and also from ten heavy elements including iron and copper. The importance of the result in the case of carbon and oxygen lies in the question, fundamental to the whole problem of nuclear architecture, whether atoms of even atomic number and with mass a multiple of 4, can be

[1] Proton is the name suggested by Rutherford (Brit. Ass. 1920) for the hydrogen nucleus.
[2] *Phil. Mag.*, **48**, 509 (1925); Chadwick, *ibid.*, (7) **2**, 1056 (1926).
[3] Atomzertrummerung, Leipzig (Akad. Verlagsges.) 1925.

disintegrated to yield hydrogen nuclei or whether these nuclei are not simple multiples of helium nuclei.[1] The divergences of opinion and fact between the Cambridge and the Vienna schools are such, as yet, that no definite decision in these matters is possible.

The Atomic Concept of Energy: The early years of the present century brought a revolutionary change in the scientific attitude towards energy. The concept of energy as a continuum was found by Planck in 1900 to be inadequate to account for the facts of black body radiation. He therefore proposed a hypothesis of discontinuous emission of radiation. In 1902, the investigation of the photoelectric effect by Lenard, led to the astonishing result that electrons, liberated from metal plates by impinging ultraviolet light, had velocities which were *independent of the intensity* of the light, but dependent on the frequency of the light and increasing in velocity with increase of the frequency. If the electronic velocities were measured by the potential V required to prevent all the liberated electrons from leaving the illuminated plate it was found that V varied linearly with the frequency of the light

$$V = C\nu + V_0, \tag{1}$$

where C and V_0 are positive constants, V_0 characteristic of the metal, C independent of the metal and the same for all. If we multiply equation (1) by e, the electronic charge, and rearrange we obtain

$$e(V + V_0) = Ce\nu.$$

Now since eV is an energy quantity, being the kinetic energy of the electrons leaving the plate with the highest velocity, it follows that the product $Ce\nu$ must also have the dimensions of energy. The frequency ν has the dimensions of reciprocal time. Hence Ce must have the dimensions of a product of energy and time, that is the dimensions of what is known in mechanics as action. As C is a universal constant and e also, the product Ce must also be a universal constant. If we assign to it the symbol h, we find, from measurements of the photo electric effect that it has the magnitude

$$h = 6.55 \times 10^{-27} \text{ erg sec.}$$

The product $h\nu$ represents a quantum of energy, the smallest unit of energy of the given frequency involved in energy change upon the Planck hypothesis. We can therefore express the relationship between the electronic velocities and the frequency of the radiation by means of the equation

$$1/2\ mv^2 = Ve = h\nu - h\nu_0.$$

The quantity $h\nu$ measures the energy absorbed by the electron from the

[1] The case of oxygen is less definite in this connection since recent spectral studies now indicate an oxygen isotope of mass 18 (Giauque and Johnson, *Nature*, **123**, 318 (1929); *J. Am. Chem. Soc.*, **51**, 1436 (1929). Aston has pointed out, however, that the quantity of such an isotope must be less than 1 part in 1000, *Nature*, **123**, 488 (1929). See also Berge, *Nature*, **124**, 14, 127 (1929), for a carbon isotope C^{13}.

radiation; $h\nu_0 = eV_0$ is the work necessary to get the electron through the surface. The potential difference V_0 is known as the "work function" for electrons passing through the surface.

The concept of individual light quanta, each with energy equal to the product of the frequency and the quantum of action, h, was definitely proposed by Einstein in 1905 and became the fundamental idea in all questions involving the interaction of light energy and matter. In the photo-electric effect, one light quantum liberated one electron. In photochemistry one light quantum activated one atom or molecule of the photo active constituents. For each elementary process, involving simultaneously light energy, one quantum of the energy in question must be either produced or consumed. The Einstein proposal was fundamental therefore in the theoretical treatment of fluorescence and chemi-luminescence; it provided the setting in which the Bohr theory of spectra and of the structure of the atom could grow. The extraordinary development which this phase of atomistics has undergone is set forth in detail in Chapter XVI.

At the outset there appeared to be a conflict between the demand of the physicist for a dynamically stable atom, requiring motions of electrons around a nucleus, and the needs of the chemist for an atom with which the facts of valence and stereo-chemical relationships might be envisaged. During the past decade these two lines of development have been more or less separately pursued. More recently there has arisen the possibility of a fusion of the two in a broader generalization, resulting from the application of wave mechanics to the general problem of the properties of matter. We can only trace at this stage the main outlines of this development in so far as it concerns the atomic concept of matter.

The Wave Theory of Matter: Progress in the quantum theory of energy made familiar the concept of units of energy, light quanta, or photons,[1] with the discontinuous structure hitherto characteristic of matter. The reversal of this mode of thought, the concept of material particles with the wave nature of light was proposed in 1924 by Louis de Broglie. It led to the wave mechanics of Schrödinger and to the quantum mechanics of Heisenberg, two aspects of the general problem of wave theory of matter intensively developed in the last years. The wave theory of matter assigns to each material particle a wave of a characteristic wave length bearing the same relation to its mass and velocity as was found in quantum theory for the photons. This relation is expressed in the equation

$$\lambda = \frac{h}{mv},$$

where λ is the wave length of the particle with mass m and velocity v, h being again Planck's constant.

It is of interest to point out the significance of this equation when applied to the electron, the smallest unit to which material properties have hitherto

[1] G. N. Lewis, *Nature*, **118**, 874 (1926).

been assigned. For the electron h/m has the value 7.27. If, then, we consider electrons with velocities in the range of $10^7 - 10^9$ cm. per sec., the equation indicates that such electrons should have wave lengths of the same order of magnitude as X-rays. Herein lay a possibility of experimental test, since the wave lengths of X-rays are determinable by well-known reflection methods from crystals. (See Chap. V.)

Such a test was applied by Davisson and Germer [1] successfully in 1927. They showed that a stream of electrons emitted from a hot filament was selectively reflected from a single crystal of nickel in a manner entirely analogous to the reflection of X-rays. The intensity of the reflection in a given direction was governed, as with X-rays, by the lattice structure of the crystal. With this experiment, therefore, the fusion of the corpuscular and undulatory aspects of both matter and energy was achieved. It gave a marked impetus to the examination of matter from the standpoint of wave theory.

Efforts to extend these experiments to particles of atomic dimensions have not attained the decisive success of the Davisson and Germer experiments. There are, however, indications in the experiments of Knauer and Stern,[2] that the reflection of helium atoms may be in accord with wave theory.

It is, however, in the reconciliation of quantum theory with the facts of chemistry that the most significant advances of the wave theory to the chemist may be anticipated. Mention may be made in this connection of the quantum mechanical treatment of the problem of combination between two atoms and the study, by London,[3] of the homopolar binding as a pairing in a molecule of two electrons, the electrons being unpaired in the atoms from which the molecule was produced. This postulate of the Lewis theory of atomic and molecular structure thus returns again in the new quantum mechanics. The chemical valence of an atom, according to London,[4] is determined by the number of its unpaired electrons.

That wave mechanics may revolutionize our knowledge even of the elements is evident from the recent predictions by Hund and later by Dennison [5] on the basis of quantum mechanics, of the existence of two forms of hydrogen molecules. The molecules are distinguished from each other by the spin of the two nuclei, the spin being such as to give wave functions symmetric in the one case and antisymmetric in the other. This prediction has now been experimentally confirmed by Bonhoeffer and Harteck [6] who have shown that the equilibrium mixture of the two, predicted by Dennison, at room temperatures (25 per cent Symmetrical: 75 per cent Antisymmetrical) is displaced at the temperature of liquid hydrogen in presence of active charcoal towards

[1] Davisson and Germer, *Nature*, **119**, 558 (1927); *Phys. Rev.* (2), **30**, 705 (1927).
[2] Knauer and Stern, *Z. Physik*, **53**, 779 (1929).
[3] Heitler and London, *Z. Physik*, **44**, 455 (1927).
[4] London, *Z. Physik*, **46**, 455 (1928); **50**, 24 (1928).
[5] Hund, *Z. Physik*, **42**, 93 (1927); Dennison, *Proc. Roy. Soc.*, **115A**, 483 (1927).
[6] Bonhoeffer and Harteck, *Sitz. ber. Pruess. Akad.* (1929); *Z. physik. Chem.*, **4B**, 113 (1929).

the direction of the symmetrical (termed by Bonhoeffer, Parahydrogen), so that, at these temperatures, the gas leaving the surface of the charcoal is at least 99.7 per cent para-hydrogen. This form is the lower in energy content. Specific heat measurements of Eucken [1] confirm this. Bonhoeffer and Harteck have examined the properties of para-hydrogen in detail. At the boiling point of ordinary hydrogen, $T = 20.39°$ K. it has a vapor pressure of 787 mm. At the triple point, $T = 13.95°$ K. the corresponding vapor pressures are $P_{\text{ord.}} = 53.9$ mm., $P_{\text{para}} = 57.0$ mm. Para-hydrogen at room temperatures and ordinary pressures is quite stable in glass vessels. Its slow return to the equilibrium mixture has been followed over a period of months. In presence of suitable catalysts, notably, platinum black, the para-modification reverts immediately to the equilibrium mixture. At higher temperatures in glass vessels the para-hydrogen becomes less stable and reverts at temperatures in the neighborhood of 1000° C. rapidly to the equilibrium mixture, even in glass tubes. The activation energy of conversion is over 50,000 calories although the heat of conversion of one form to the other is only 329 calories at 0° K. Such modifications in our knowledge of well-known molecular species by reason of the newer developments in the wave theory of matter are sufficient evidence of the importance of the modern developments in theoretical physics for the modern physical chemist.

[1] Eucken, *Naturwiss.*, **17**, 182 (1929).

CHAPTER II

THE ENERGETICS OF CHEMICAL CHANGE

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It is not possible to define completely any system by sole reference to the material content of the system, its atomic or molecular constituents. Associated with matter, independent of the fixed and unchangeable attributes of mass and form, are other properties which change with circumstances. Thus, for example, the temperature, pressure, heat content, motion, electrical potential, color may vary, without variation in the actual atomic or molecular content of the system. The properties of a copper rod when hot differ from those of a cold rod, those of a metal at high electrical potential from those of a metal uncharged. Motion and position convey definite properties to matter as can be illustrated by means of a rifle bullet or an avalanche. Even at a constant temperature the form of matter may vary. Gaseous, liquid and solid mercury either separate or coexistent are possible at a given temperature. The compression to which a given system is subjected may determine the changes which such a system will undergo. These variables, to which all forms of matter are subject and from which they cannot be entirely dissociated, are all energy variables of material things.

Every variation in the properties of a given species of matter is to be attributed to a variation of one or more of several energy variables. These energy variables are convertible, one into the other, matter being the medium whereby such conversion is effected. Thus, heat energy is convertible into the energy of motion, the increased motion of the particles receiving such heat energy. Conversely, motion may be converted into heat energy by friction as was emphasized by Count Rumford in his inquiries concerning the heat resulting from the boring of cannon, or as demonstrated by Davy in the production of water by the friction of ice. Electrical energy can be expended in the production of heat energy or in the production of chemical change whereby chemical energy may be produced. Chemical energy is the source of most of our heat energy and is an instrument in the production of electrical energy. Many chemical actions are productive of light or may be made to produce it by way of other energy forms. This interchangeability of the forms of energy suggests therefore that energy, like mass, may be indestructible, but multiform or protean. Before, however, this concept of interconvertibility of energy can be examined in its quantitative aspects, the method of definition of energy must be examined in some detail.

The Definition of Energy: Every change in the condition of matter is to be ascribed to the operation of one or other forms of energy. The energy is composite of two factors, an intensity factor and a capacity factor, and is, indeed, the product of these two factors. The intensity factor is the measure of the resistance offered to the change of condition resulting from the operation of the energy. The energy can only operate when this resistance is either withdrawn or overcome. Such an intensity factor tending to produce a change is known as a force. A force, overcoming a resistance to an extent which we may designate as the capacity factor, performs work, expends energy. With a given force, the energy expended or the work performed varies directly as the capacity factor. In the production of motion the energy expended depends, therefore, on the force required to produce motion against the resistance and on the distance through which the object acted upon is moved. In the raising of an object of mass m against gravity, g, through a height h, the force exerted in opposition to gravity is mg and the capacity factor is the height h. The energy expended becomes, therefore, the product mgh. In the production of a volume change dv in any body against an external pressure p, the intensity factor or force, p, acts through a volume dv which is the capacity factor; the work done or energy expended is the product of the two factors, pdv. All energy changes of whatever form may be similarly resolved into two such factors.

The unit of energy in the c.g.s. system of units is the *erg*. It is the energy associated with a force of one *dync* acting through one centimeter. A dyne is the force which, acting for one second on one gram, produces a velocity of one cm. per second in the body upon which the force is impressed. It is related to the action of gravity upon a mass. Gravity produces an acceleration of 980.6 cm. per sec. when acting upon a mass at sea-level and 45° latitude. The weight of one gram divided by $g = 980.6$ cm. per sec. is equivalent to one dyne. If the pressure of the atmosphere be defined as the pressure of 760 mm. of mercury under standard conditions, it may be expressed in dynes per sq. cm.

$$1 \text{ atmos.} = 76 \times 13.59 = 1033.3 \text{ grams per sq. cm.}$$
$$= 980.6 \times 1033.3 = 1013300 \text{ dynes per sq. cm.}$$

The First Law of Energetics

The Mechanical Equivalent of Heat: The first statement of the equivalence of heat and mechanical work is to be attributed to Mayer, 1842, who also attempted to ascertain the proportionality factor connecting the two energy quantities. Carnot (died 1832), in a posthumous publication, enunciated the same principle: "Heat is simply motive power or motion which has changed its form, for it is but a movement amongst the particles of a body. Whenever motive power is destroyed, an equivalent quantity of heat is produced; and, reciprocally, whenever heat is destroyed, motive power is developed." Mayer calculated the work involved in the expansion process when the specific heat of a gas is measured at constant pressure, this work, w, being then equated to

the difference of the specific heats at constant pressure and constant volume, $c_p - c_v$ by the proportionality factor J, the mechanical equivalent of heat.

$$w = J(c_p - c_v).$$

The assumption involved in this calculation, namely, that heat energy and mechanical energy are equivalent, received its first experimental test by Joule, 1843–1880. He measured the heat produced q by most divergent mechanical processes and showed that in each case the proportionality factor, J, was approximately constant,

$$w = Jq.$$

Joule's experiments included the following:

(1) The heat produced when various liquids, water, oil and mercury, were stirred was compared with the work involved in producing the stirring by falling weights.

(2) The heat produced in a coil of wire by induction currents set up by rotation of the wire between the poles of an electromagnet was compared with the work done by falling weights in rotating the coil. The heat produced was measured by the rise in temperature of water in which the coil was rotated.

(3) The heat produced by compression of water through narrow openings or capillaries was compared with the work required to drive the water through the openings or capillaries.

(4) The heat produced by compressing air to 22 atmospheres was compared with the work of compression.

(5) The heat produced by the passage of an electric current through a coil of wire immersed in a calorimetric fluid was compared with the energy of the current consumed.

Joule concluded that "772 lbs. falling one foot would heat a pound of water one degree." Transformed into modern units Joule's measurements gave approximately

$$J = 4.17 \times 10^7 \text{ ergs per } 15° \text{ cal.}$$

The fact that independent methods of producing heat gave closely concordant values for J constituted the desired proof of the law of equivalence of heat energy and mechanical energy.

These early measurements have been repeated at intervals with greater refinements of technique. Rowland (1879), Miculescu (1892) and Reynolds and Moorby (1898) have determined J by the water-stirring method. Greater accuracy is achieved with the electric heating method, which has been employed by Griffiths (1893), Schuster and Gannon (1895), Callendar and Barnes (1902), Dieterici (1905). The former method gives a mean value

$$1\ (15°)\ \text{cal.} = 4.1829 \times 10^7 \text{ ergs}\ ^1$$

in good agreement with the determination of Miculescu, namely, 4.183×10^7 ergs.[1] By the electrical method the mean value is

$$1\ (15°)\ \text{cal.} = 4.1809 \times 10^7 \text{ ergs}\ ^2$$

[1] A. W. Smith, *U. S. Weather Review*, **35**, 458 (1907).
[2] A. W. Smith, *Phys. Rev.*, **33**, 173 (1911).

when the electromotive force given by the Weston cell at 20° C. is defined by international agreement as 1.0183 volts. The average of these two determinations gives

$$1\ (15°)\ \text{cal.} = 4.182 \times 10^7\ \text{ergs.}$$

Assuming that, with the new definition of electromotive force just mentioned, the volt-coulomb = 1 joule = 10^7 ergs, it follows that

$$1\ (15°)\ \text{cal.} = 4.182\ \text{joules};\ 1\ \text{joule} = 0.2391\ \text{cal.}$$

Since a pressure of 1 atmosphere = 1013300 dynes per sq. cm.,

$$1\ \text{cc.-atmos.} = 1013300\ \text{ergs} = 0.10133\ \text{joules.}$$

For a perfect gas, it will be shown that the fundamental equation connecting pressure, volume and temperature is, for one mol,

$$pv = RT,$$

where R is the gas constant. On the absolute temperature scale, 0° C = 273.1°. For one mol of gas under standard conditions the accepted value of v = 22412 cc. Hence,

$$R = \frac{22412 \times 1}{273} = 82.07\ \text{cc. atmos. per degree.}$$

When transformed into the units of heat energy with the data already supplied

$$R = 1.9885\ \text{calories per degree}$$

or

$$R = 8.316\ \text{joules per degree.}$$

The Law of Conservation of Energy: This law, the first law of energetics, of which the equivalence of heat and mechanical energy is a special case, was definitely enunciated by Helmholtz in a publication "Über die Erhaltung der Kraft,"[1] 1847. In this contribution, Helmholtz demonstrated that the law of equivalence of heat and mechanical energy was a direct consequence of the century-old experience of investigators that it is impossible to produce a perpetual motion machine which, without expenditure of energy, shall produce energy. Definite proof of the impossibility of constructing such a machine cannot be achieved. It is necessary to rely upon the cumulative experience of investigators that the search for such a machine is fruitless. Furthermore, by assuming the impossibility of perpetual motion of this type, conclusions may be drawn which may be verified and, in their turn, be employed for the discovery of further facts or laws. Thus is attained the definite and general belief as to the truth of the fundamental law.

Helmholtz pointed out that if the mechanical equivalent of heat were not an invariable quantity, it would be possible by suitable coupling of two processes

[1] *Ostwald's Klassiker*, No. 1.

of energy transformation, heat into mechanical work, to arrange that the heat produced in the stage of energy consumption should be more than sufficient to produce, in the second stage of the process, the same amount of energy as was consumed in the first stage. A perpetual motion machine would result. Heat energy would be continuously produced without the expenditure of any other energy form. The impossibility of such a perpetual motion machine compels our belief in the exact equivalence of heat and mechanical energy. Helmholz concluded therefore that: "In all processes occurring in an isolated system, the energy of the system remains constant."

The energy of a system is a function only of the state of the system at the given moment irrespective entirely of its past history, the manner or method of its origin. It is especially to be emphasized that this independence of past history refers only to systems whose identity is complete in all except the element of time. It is not enough that the atomic or molecular make-up shall be the same, for this may be secured even though the energies of the systems differ widely. Thus, for example, stick lead and electrolytic lead might be identical as to atomic content, pressure, temperature, volume and the like, but be different in energy content by reason of state of division, size of crystal and the like. Only with complete identity in all factors except time can it follow that the energy is a function of the momentary state. The energy change is then a function of the initial and final states of the system. For, if it were possible to effect a change in any system from state A to state B such that the energy change involved was dependent on the path by which the change was achieved, it would again be possible to construct a perpetual motion machine. All that would be necessary would be that one such method of conducting the change could be reversed. Then, by a suitable coupling of two processes,

$$A \rightarrow B \text{ by path I,}$$
$$B \rightarrow A \text{ by path II,}$$

if the energy produced in path I were larger than that consumed in path II, the system would be, on completion of the reverse process, in its initial state and a surplus of energy would be available. By repetition of the process, energy could be continuously produced—a perpetual motion would be possible. This is denied by human experience as embodied in the first law of energetics.

The Internal Energy of a System: The change from state A to state B of a given system is therefore accompanied by a perfectly definite energy increment which we may designate by ΔU and define by the expression

$$\Delta U = U_B - U_A.$$

In such case, U_B and U_A represent the energies of the system in states B and A respectively. They may be more definitely designated as the internal energies of the system in the two states. They are energy quantities of unknown absolute magnitude. They include the energy resultant from such factors as motion of the molecules, position of the molecules, molecular attraction, intra-molecular forces, intra-atomic vibrations, chemical and other

unascertained forces. While, however, the absolute magnitude of such internal energy is not ascertainable, the change in such is definite and unchangeable for any given process of change.

Any such change in the internal energy of a system can only be achieved with a simultaneous change in the energy of surrounding systems, since the law of conservation of energy *must* be obeyed. An increment in internal energy of the system is secured, therefore, at the expense of a decrement in the energy of its surroundings. A decrement in the internal energy results in an increase of the energy of its surroundings. If we consider any process of change from state A to state B, whereby an increment of internal energy $\Delta U = U_B - U_A$ occurs, which results in the abstraction of heat, q, from the surroundings and simultaneously the performance of external work w by the system on the surroundings; then, by application of the law of conservation of energy,

$$\Delta U = q - w.$$

It has been shown that ΔU is a perfectly definite quantity for any given process, dependent only on the initial and final states, A and B. This is not true of either q or w. According as the experimental conditions change, q or w may both vary. Thus, if the process be carried out at constant volume and no other energy factors than those of mechanical energy are involved in the external work performed,

$$w = 0.$$

In such circumstances

$$\Delta U = q,$$

the whole increment of internal energy is secured at the expense of the heat of the surroundings. Ordinarily, processes are conducted, not at constant volume, but at constant pressure. In such case, a process will in general be accompanied by a volume change. The external work done by the system on the surroundings will be

$$p(v_B - v_A) = p.\Delta v,$$

p being the prevailing pressure, Δv the increase in volume of the system during the change from state A to state B. The heat q abstracted from the surroundings will be increased by an amount equal to the quantity $p\Delta v$, since

$$q = \Delta U + w = \Delta U + p\Delta v.$$

Conceivably the process may be conducted so that heat is neither gained nor lost by the system. Such a process is known as an *adiabatic* process. The quantity q is then zero. The work performed by the system on the surroundings must then be done at the expense of the internal energy of the system, or

$$\Delta U = - w.$$

It will later be shown that the quantity w may be composite of several forms of energy including mechanical, electrical, radiant energy and the like, and

that, furthermore, the magnitude of such work performed may vary with the mode of conduct of the process.

It is thus evident that while U, the internal energy of the system, is a single-valued function of its several variables, pressure, temperature, volume and the like, dependent only on its state at the moment, this is not true concerning the quantities q and w. Whereas the small change of internal energy, dU, has the properties of a complete differential,

$$dU = \frac{\partial U}{\partial x}dx + \frac{\partial U}{\partial y}dy + \frac{\partial U}{\partial z}dz + \cdots,$$

where x, y, z, etc., are the several variables, the same is not true of the heat absorbed or external work performed by the system when such change in internal energy occurs. These may vary extremely, provided always that the law of energy conservation is satisfied,

$$\Delta U = q - w.$$

The quantities q and w are dependent *entirely* on the path by which the process is achieved.

The Heat Content of a System: Returning now to consideration of a process involving an increase in internal energy, heat absorption from the surroundings and a volume change v_A to v_B against a constant external pressure p. The first law of energetics demands that

$$\Delta U = U_B - U_A = q - p(v_B - v_A).$$

This may be transformed thus:

$$(U_B + pv_B) - (U_A + pv_A) = q.$$

In this case the heat, q, absorbed by the system is evidently defined by the initial and final states of the system. If we define a quantity

$$H = U + pv$$

and term this quantity, H, the heat content of the system, the equation becomes

$$H_B - H_A = q = \Delta H.$$

It will be noted that the quantity ΔH, like ΔU, is dependent only on the initial and final states of the system. The heat content of the system, H, like U, is a single-valued function of its several variables.

The Heat Capacity of a System: We may define the mean heat capacity, $\bar{c}$, of a system between two temperatures as the quantity of heat necessary to raise the system from the lower to the higher temperature divided by the temperature difference,

$$c(T_2, T_1) = \frac{q}{T_2 - T_1}.$$

Since the heat capacity is known to vary with temperature, the true heat capacity at a given temperature may be defined by the differential expression

$$c = \frac{dq}{dT}.$$

The heat capacity may be determined either at constant volume or constant pressure, the magnitude of the heat capacity being dependent on the mode of experimentation. In the determination of heat capacity at constant volume, none of the absorbed heat is employed in the performance of external work. Hence, the heat absorbed, q, is equal to the increase in internal energy. We may, therefore, define heat capacity at constant volume per mol. of substance by the equation

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v.$$

At constant pressure, since

$$q = \Delta U + w,$$

the heat absorbed to produce a given rise of temperature will be greater by an amount equivalent to the external work performed by the system on the surroundings. Hence, we may define the mean heat capacity at constant pressure thus:

$$\bar{c}_p = \left(\frac{q}{T_2 - T_1}\right)_p = \left(\frac{\Delta U + p\Delta v}{T_2 - T_1}\right)_p = \left(\frac{\Delta H}{T_2 - T_1}\right)_p$$

and, for the true molecular heat capacity at constant pressure,

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p.$$

The Heat of Chemical Reaction: Chemical reactions are in general accompanied by absorption of heat from or evolution of heat to the surroundings; they are either endothermic or exothermic. For a reaction occurring at constant volume, the heat absorbed or evolved is equal to the change in internal energy of the system, since no external work is performed. Hence $-\Delta U$ is a measure of the number of calories evolved in the reaction, or, in other words, a measure of the heat of reaction at constant volume. A thermochemical result of this type may be illustrated by the equation

$$CO + H_2O = CO_2 + H_2 + 10500 \text{ cals.}$$

Hence

$$\Delta U = -10500 \text{ cals.}$$

For reaction at constant pressure, p, accompanied by a volume increase, Δv, the heat absorbed, q, is equal to the increase in internal energy plus the external work performed,

$$q = \Delta U + p\Delta v = \Delta H.$$

At constant pressure, therefore, $-\Delta H$ is a measure of the calories produced in the given reaction,

$$C + O_2 = CO_2 + 97000 \text{ cals}; \quad \Delta H = -97000 \text{ cals}.$$

The Constancy of the Heat of Reaction: Hess's Law: Since, in any process, both quantities ΔU and ΔH are dependent on the initial and final states of the system only and are independent of the path between, it follows that both the heat of reaction at constant volume and that at constant pressure, being numerically equal but opposite in sign to the increase in internal energy, ΔU, and that of heat content, ΔH, respectively, must also be defined by the initial and final states of the system independent of the path taken. In other words the heat evolved in any chemical reaction is independent of the manner in which the reaction is achieved whether in one or many steps. Thus, in the combustion of carbon to carbon dioxide the heat of reaction at constant pressure, $-\Delta H_1$, is equal to that for the two-stage process: (*a*) carbon to carbon monoxide, $-\Delta H_2$, (*b*) carbon monoxide to carbon dioxide, $-\Delta H_3$. Thus,

$$\begin{aligned} C + O_2 &= CO_2; & -\Delta H_1 &= 97000 \text{ cals.}, \\ C + \tfrac{1}{2}O_2 &= CO; & -\Delta H_2 &= 29000 \text{ cals.}, \\ CO + \tfrac{1}{2}O_2 &= CO_2; & -\Delta H_3 &= 68000 \text{ cals.}, \\ & & -\Delta H_1 &= (-\Delta H_2) + (-\Delta H_3). \end{aligned}$$

This consequence of the first law of energetics, which as will be shown later (Chapter VI) is of great utility in the science of thermochemistry, was first enunciated by Hess in 1840, prior to the formulation by Mayer and Joule of the law of conservation of energy, of which it is a special case. The law forms the theoretical basis of the classical experimental work of Thomsen and Berthelot on the thermal magnitudes of a wide variety of chemical compounds. For, the law of Hess involves as corollaries a number of useful conclusions. Thus, the heat of formation of a compound must be independent of the manner of its formation; the heat of reaction must be independent of the time consumed in the process; the heat of reaction must be equivalent to the sum of the heats of formation of the products of the reaction less the sum of the heats of formation of the initial reactants. The experimental methods of thermochemistry, the details of typical results obtained and of the methods of calculation will be given in a succeeding chapter (Chapter VI).

Heat of Reaction and Temperature: Kirchhoff's Law: The heat of reaction of a given process varies with the temperature, the mode of variation of which may be elucidated by consideration of a given process,

$$A \rightarrow B,$$

occurring at two temperatures T and $T + dT$ differing infinitesimally. For simplicity let the several processes be assumed to occur at constant volume. In the first place the reaction may be assumed to occur at temperature T whereby q calories of heat are yielded to the surroundings. The system B may

now be raised from T to $T + dT$. This will require absorption of heat by the system equal to $C_v'.dT$, where C_v' is the heat capacity of the system B at constant volume in the given small temperature interval. In the second place, the process may be achieved by another path. The system A may be raised from T to $T + dT$ whereby analogously the heat absorbed will be $C_v.dT$. The reaction A to B may now be conducted at the temperature $T + dT$ whereby a heat evolution equal to $q + dq$ calories occurs. From the law of conservation of energy, the heat change from A at temperature T to B at temperature $T + dT$ is independent of the path by which it is achieved; otherwise, a perpetual motion machine could be realized. Hence, assigning positive values to heat absorbed by the system and negative values to heat given to the surroundings, we obtain by equating the two modes of procedure

$$-q + C_v'dT = C_vdT - (q + dq),$$

whence

$$dq = (C_v - C_v')dT$$

or

$$\frac{dq}{dT} = C_v - C_v'.$$

Since, at constant volume, q, the heat evolved in a process is equal to $-\Delta U$, we may write the equation

$$\frac{d(\Delta U)}{dT} = C_v' - C_v = \Delta C_v.$$

In a similar manner it may be shown that (see Chapter VI), operating at constant pressure instead of at constant volume,

$$\frac{d(\Delta H)}{dT} = \Delta C_p,$$

where ΔC_p represents the heat capacity of the products less that of the reactants. The temperature coefficient of the heat of reaction under any circumstances is therefore equal to the change in the heat capacity which the system undergoes in those circumstances. This law was first deduced by Kirchhoff[1] in 1858. It is applicable alike to chemical reactions and to all those processes such as fusion, vaporization and the like which we more usually term physical processes. More recently the applicability of the law in cases of sub-atomic nature has been demonstrated.

The Thomsen-Berthelot Principle: An Erroneous Concept of Chemical Affinity: The idea underlying the comprehensive investigations of Thomsen (1854 onwards) and of Berthelot in the domain of thermochemistry was the assumption that the heat of reaction was a direct measure of chemical affinity. In the words of Berthelot, "every chemical change which takes place without the aid of external energy tends to the production of that system which is accom-

[1] *Pogg. Ann.*, **103**, 454 (1858).

panied by the development of the maximum amount of heat." This principle is wrong. Many reasons may be adduced to prove its incorrectness. If the principle were true, only exothermal reactions could take place unless external energy were simultaneously utilized. For, endothermic reactions would indicate a negative affinity or a repulsion. The existence of endothermic reactions had, therefore, to be explained by the proponents of the theory by assumption of the operation of secondary physical factors. Thus, the spontaneous solution of many salts in water, frequently endothermal, is apparently a contradiction of the Thomsen-Berthelot principle. It was "explained" that although the net observed heat effect was negative, the positive value, due to the affinity proper, was masked by secondary thermal magnitudes due to physical changes, e.g., the change of the solid salt to the fluid condition in solution. Such assumptions, impossible of test by measurement, only served to complicate what is, as will be shown, a very simple quantity, the chemical affinity of a system. The Thomsen-Berthelot principle implied, moreover, that reactions should proceed to completion in that direction in which exothermicity was developed. This had been definitely disproved by the researches of Berthollet at the beginning of the nineteenth century; the concept of balanced actions became indispensable when the Law of Mass Action was put forward by Guldberg and Waage in 1864. Balanced actions and equilibrium involve the simultaneous occurrence of exothermal and endothermal changes at one and the same temperature.

It will emerge in the subsequent discussion that the heat of reaction is not the true thermodynamic criterion for chemical reaction. On the contrary, the change of free energy, the capacity of the system to do chemical, electrical or mechanical work will be shown to be the correct measure of the driving force of a reaction. In certain special, but accidental, cases, the heat of reaction and the free energy of the process may be equal. In the majority of cases this will not be true. To demonstrate the correct relationship between these two magnitudes the first law of energetics is insufficient. New limitations on the convertibility of energy must first be discussed and these will lead to a second law of energetics. In the meantime it may be emphasized that the law of conservation of energy gives no information as to the *direction* of energy changes. It only insists that, whatever the direction of change, no energy shall be lost or gained by the system taken as a whole.

Applications of the First Law to Gases

The Internal Energy of an Ideal Gas: It will be shown subsequently that in general a gas may be defined by reference to two of the three variables, pressure, volume and temperature, any two of which will give the third a definite value. Since the internal energy of a substance is a function of its state at any given moment, it follows that the small change in internal energy dU of such a gas may be expressed by an equation of the form

$$dU = \frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial v} dv,$$

in which case v and T are chosen as the two variables. Now $\partial U/\partial T$ is the heat taken up by one mol. of gas when it is heated one degree without performing external work, for then

$$\Delta U = q.$$

This, however, is really the heat capacity at constant volume. Hence

$$\frac{\partial U}{\partial T} = C_v.$$

We may therefore write the above equation in the form

$$dU = C_v dT + \left(\frac{\partial U}{\partial v}\right) dv.$$

Hence, also, from the first law

$$q = C_v dT + \frac{\partial U}{\partial v} dv + w.$$

Now the work done in an expansion dv of a gas at constant pressure, p, $= pdv$. Hence

$$q = C_v dT + \frac{\partial U}{\partial v} dv + pdv.$$

If now the temperature change accompanying the expansion of a gas in a thermally insulated system (i.e., $q = 0$) against zero pressure (i.e., $pdv = 0$) be determined, such a temperature measurement will yield information relative to the change of internal energy with volume. This experiment was first carried out by Gay-Lussac and later by Joule, by allowing the gas from one vessel, I, to stream into an evacuated vessel, II, until pressure equilibrium was established in the complete system I + II. By having the system immersed in water in a calorimeter any temperature variation could be noted. The first experiments of this type led to the conclusion that dT was equal to zero. It was therefore concluded that, for such a system,

$$\frac{\partial U}{\partial v} = 0.$$

It follows, therefore, that for all such gaseous systems as would give this experimental result the internal energy would be independent of the volume, dependent only on the temperature of the system.

More accurate measurements, subsequently performed by Joule and Thomson (later Lord Kelvin), established the fact that this conclusion was incorrect for all real gases, but that it was approached the more closely the more the gas approached a condition of ideality. The lower the initial pressure in vessel I, or the higher the experimental temperature T, the more nearly did dT approach zero and therefore the more nearly did $\partial U/\partial v$ approach zero.

The real thermodynamic criterion to be fulfilled by any ideal gas may be learned by a study of the experimental method employed by Joule and Thomson to determine the temperature changes accompanying an expansion of a real gas. The change from a high pressure p_1 to a lower pressure p_2 was made to occur slowly by interposing a resistance to the gas flow. A porous plug divided the region of high pressure from that of low pressure. As the gas passed through the plug under compression on the high pressure side, p_1, the volume on the low pressure side was increased. Diagrammatically this may be illustrated in Fig. 1.

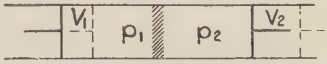

FIG. 1

The work done on the gas at high pressure p_1 for a gram mol. of the gas at volume v_1 compressed through the plug is obviously p_1v_1. On the low pressure side correspondingly the work done by the gas on the surroundings is p_2v_2. Now if Boyle's Law be obeyed by the gas in question,

$$p_1v_1 = p_2v_2,$$

it is evident that the system as a whole has performed no external work,

$$w = 0.$$

In a thermally insulated system q also is equal to zero. Under such circumstances

$$-C_vdT = \left(\frac{\partial U}{\partial v}\right)dv.$$

Whence, if $dT = 0$, it follows also that

$$\left(\frac{\partial U}{\partial v}\right)_T = 0.$$

Hence an ideal gas may be defined thermodynamically as a gas fulfilling two conditions,

$$(a) \quad \left(\frac{\partial U}{\partial v}\right)_T = 0,$$

$$(b) \quad pv = \text{constant}.$$

Real Gases: The Joule-Thomson Coefficient: For real gases, in general, p_1v_1 will not be equal to p_2v_2. The external work performed by the system as a whole upon the surroundings will be

$$p_2v_2 - p_1v_1 = w.$$

According to the first law, for a process without heat absorption, a so-called *adiabatic* process,

$$\Delta U = U_2 - U_1 = -w = p_1v_1 - p_2v_2.$$

Hence

$$U_2 + p_2v_2 = U_1 + p_1v_1.$$

This equation may be transformed into

$$H_2 = H_1,$$

since

$$H = U + pv.$$

The free expansion of a real gas occurs, therefore, not with constant internal energy U but with constant heat content H. The Joule-Thomson coefficient is therefore definable as the change in temperature produced when the gas expands at unit pressure differential and constant heat content, or mathematically

$$k = \left(\frac{\partial T}{\partial p}\right)_H.$$

The Joule-Thomson coefficient for a number of gases under stated conditions is given in the following table.

TABLE I

JOULE-THOMSON COEFFICIENTS

		$k = \frac{T}{P}$ at Pressures				
Gas	$t°$ C.	0–6	2	10	15	40 atm.
Hydrogen	6.8	−0.030[a]				
	90.1	−0.044[a]				
Carbon Dioxide	0	1.35[a]				1.46[c]
	20	1.14[a]	1.21[b]	1.31[b]	1.37[b]	1.20[c]
	40	0.96[a]				1.04[c]
	100	0.62[a]				
		$P = 0$	25	50	100	150 Kg. cm.^{2}
Air[d]	−55	0.44	0.40	0.3	0.28	0.18
	0.6	0.27	0.25	0.24	0.19	0.16
	49	0.20	0.18	0.17	0.15	0.12
	150	0.09	0.09	0.07	0.06	0.05
	250	0.02	0.02	0.02	0.01	0.01
		$P = 1$	4.5	6.4 m. Hg		
Air[e]	0	0.399	0.378	0.359		
	50	0.298	0.278	0.270		
	100	0.224	0.210	0.213		

[a] Joule-Thomson.
[b] Natanson, *Wied. Ann.*, **31**, 502 (1887).
[c] Kester, *Phys. Rev.*, **21**, 260 (1905).
[d] Noell, *Forsch. Arbeiten* No. 184 (1916).
[e] Hoxton, *Phys. Rev.*, **13**, 438 (1919).

Now since in the free expansion of real gases, $H = U + pv$ is constant, i.e., $dH = d(U + pv) = 0$, and since H is also a single-valued function of any two of the variables, p, v, and T, that is,

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp,$$

it follows that, since $dH = 0$,

$$\frac{dT}{dp} = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{C_p}.$$

In other words the magnitude of the Joule-Thomson coefficient is determined by the variation in the quantity H with pressure at constant temperature since C_p is a definite numerical quantity.

The variation of H with pressure is determined by the respective variations of U and pv of which the quantity H is composed. For the majority of gases, with hydrogen and helium as exceptions, it has been experimentally determined that, with increasing pressure and at constant temperature, the product pv at first decreases and then increases. For moderate pressures, therefore, p_2v_2, the pressure-volume product on the low pressure side of the plug, will be greater than p_1v_1 for all gases excepting hydrogen and helium. Hence, in the porous plug experiment, the net external work done by the system upon the surroundings will be positive at moderate pressures for all gases except hydrogen and helium. In an adiabatic system cooling would therefore occur. At higher pressures, when pv has increased sufficiently with increasing pressure, p_2v_2 will be less than p_1v_1 and the effect of Boyle's Law will be to cause a warming up of the system in passage through the plug.

As far as the variation of U with pressure is concerned, with all real gases, the effect of expansion will be to produce a cooling of the gas. The molecular constituents of real gases exert an attractive force upon one another which is overcome when an expansion of the gas occurs. In every case therefore, under adiabatic conditions, the energy required in overcoming these attractive forces must come at the expense of the kinetic energy of the gas molecules and cooling will be produced.

The total observed effect will be composite of these two factors. They must operate in such manner that the heat content H shall be invariable throughout the process.

Rose-Innes has shown that the experimental measurements of Joule and Thomson could be represented by an equation of the type

$$\frac{dT}{dp} = \frac{a}{T} + b.$$

For air and carbon dioxide characteristic constants, a and b, were obtained,

positive in sign. For hydrogen b was negative. In this last case evaluation of the constants $a = 64.1$, $b = -0.331$ indicated that at $T = 194°$ K. or $-79°$ C. the quantity dT/dp became zero. Below this temperature, the Joule-Thomson coefficient is positive, that is, cooling is produced in hydrogen below this temperature. This is in agreement with experimental investigations of Olzewski who showed that below 80° C. hydrogen could be cooled by expansion. All gases, other than hydrogen and helium, probably show inversion points at temperatures above ordinary room temperatures.

Joule and Thomson found that the Joule-Thomson coefficient varied inversely as the square of the absolute temperature

$$\frac{dT}{dP} = \frac{a}{T^2}.$$

This indicates that the lower the temperature, the greater the cooling effect produced per unit pressure gradient, a conclusion which has been experimentally verified in many cases.

The influence of pressure on the magnitude of the coefficient has been studied for oxygen at 0° C. over a considerable pressure range by Vogel.[1] The cooling effect decreased from 0.260° per atm. pressure gradient at 20 atm. pressure to 0.139° at 160 atm. pressure. Over a more limited pressure range Hoxton has studied the variation in the coefficient for air. He finds also a diminution of the coefficient with increasing pressure at constant temperature, the combined effects of pressure and temperature being representable by an empirical equation

$$k = -0.1975 + \frac{138}{T} - \frac{319P}{T^2}.$$

The Joule-Thomson effect is made use of practically for the liquefaction of gases by the so-called Linde-Hampson process. The gas cooled by expansion is utilized to pre-cool the compressed gas passing through the plug. A lower temperature is thereby produced in the gas upon expansion. The cooling is thus made cumulative until finally a temperature is attained at which liquefaction occurs. The efficiency of such a process may be calculated from the known data on the heat capacities of the gases at the two pressures, the Joule-Thomson coefficient, the boiling point and the heat of vaporization of the liquefied gas, when it is remembered that the heat content of the system undergoes no change.

The Relation between C_p and C_v: It has been shown that the quantities C_p and C_v are representable by the equations

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p,$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v.$$

[1] München, 1910.

[2] *Phys. Rev.*, 13, 438 (1919).

Hence

$$C_p - C_v = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v$$
$$= \left(\frac{\partial (U + pv)}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v$$
$$= \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v.$$

Now

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial v}\right)_T dv.$$

Hence

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$$

or

$$C_p - C_v = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p + p\left(\frac{\partial v}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v$$
$$= \left[p + \left(\frac{\partial U}{\partial v}\right)_T\right]\left(\frac{\partial v}{\partial T}\right)_p.$$

For an ideal gas it has been shown that

$$\left(\frac{\partial U}{\partial v}\right)_T = 0.$$

Hence, for such gases

$$C_p - C_v = p\left(\frac{\partial v}{\partial T}\right)_p.$$

Employing the equation of state for an ideal gas

$$pv = RT,$$

it follows that

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p}.$$

Hence, for such gases

$$C_p - C_v = R.$$

Isothermal Expansion of an Ideal Gas: From the first law of energetics,

$$\Delta U = q - w,$$

it has been shown that ΔU is independent of volume change for an ideal gas, Hence, in the expansion of such a gas

$$q = w.$$

For an infinitesimal volume change dV at pressure p

$$q = pdV.$$

For a finite volume change, V_1 to V_2,

$$q = \int_{V_1}^{V_2} pdV.$$

Assuming for 1 mol. of gas that $pV = RT$, it follows that

$$q = \int_{V_1}^{V_2} RT\frac{dV}{V} = RTln\frac{V_2}{V_1}.$$

For an ideal gas we may also put $p_1V_1 = p_2V_2$, where p_1 and p_2 are the pressures concerned. The heat absorbed in the isothermal expansion becomes therefore

$$q = RTln\frac{p_1}{p_2}.$$

Adiabatic Expansion of an Ideal Gas: In this case, since the process is adiabatic,

$$q = 0.$$

Hence

$$\Delta U = -w = -p\Delta V.$$

Since external work is done by the system on the surroundings, the temperature of the gas must fall. The magnitude of the decrease in temperature may be calculated thus:

Since

$$\Delta U = C_v.\Delta T \qquad \text{and} \qquad pV = RT,$$

$$C_v.\Delta T = -p.\Delta V,$$

or, in the limit,

$$C_v.dT = -pdV,$$

whence on integration

$$C_v(T_1 - T_2) = \int_{V_1}^{V_2} pdV.$$

Alternatively

$$C_v\frac{dT}{T} = -R\frac{dV}{V}$$

or

$$C_vdlnT = -RdlnV$$

or

$$C_vln\frac{T_2}{T_1} = Rln\frac{V_1}{V_2}.$$

Now, since $C_p - C_v = R$, and putting $C_p/C_v = \gamma$,

$$ln \frac{T_2}{T_1} = \frac{R}{C_v} ln \frac{V_1}{V_2},$$

$$ln \frac{T_2}{T_1} = (\gamma - 1) ln \frac{V_1}{V_2}$$

or

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}.$$

Since $p_1 V_1 = RT_1$ and $p_2 V_2 = RT_2$, it follows that

$$p_1 V_1^{\gamma} = p_2 V_2^{\gamma}$$

or

$$p_1^{1-\gamma} T_1^{\gamma} = p_2^{1-\gamma} T_2^{\gamma}.$$

Cyclic Processes: A system which, upon completion of a change or series of changes, is in its original state is said to have completed a cycle. The whole process is known as a cyclic process. From the first law it follows that, since U is a single-valued function of its variables, dependent, therefore, only on the state of the system, independent of past history, for every cyclic process,

$$\Delta U = 0 = q - w.$$

If conducted at constant temperature the cycle is known as an isothermal cycle.

The cyclic process forms a useful method of studying the variation of matter when subjected to variations of energy content. The most celebrated of such cyclic processes is known as the Carnot Cycle.

The Carnot Cycle: This cycle comprises a four-stage process to which an ideal gas may be submitted. It was employed by Carnot to demonstrate the work available from a process of heat transfer. The cycle consists of four successive processes: (*a*) an isothermal expansion, (*b*) an adiabatic expansion, (*c*) an isothermal compression at the lower temperature produced in the previous adiabatic expansion and (*d*) an adiabatic compression whereby the ideal gas is restored to its original temperature, pressure and volume. The accompanying diagram represents the p–v relationships in such a cycle starting at the state represented by A at temperature T_2, with the sequence of changes already detailed carrying the gas through states represented by the lines (*a*) *AB*, (*b*) *BC*, (*c*) *CD* and (*d*) *DA*.

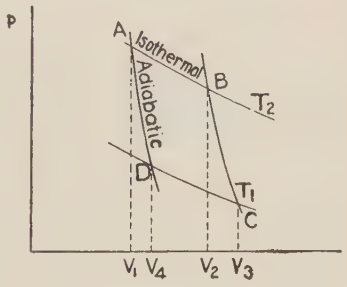

FIG. 2

The lines *AB* and *CD* represent the two isothermals, at the temperatures T_2 and T_1 ($T_2 > T_1$). The lines *BC* and *DA* represent the two adiabatics.

Let the respective p, v, T magnitudes be for A, p_1, V_1, T_2, for B, p_2, V_2, T_2, for C, p_3, v_3, T_1 and for D, p_4, V_4, T_1.

We may follow the changes occurring in the several stages thus:

Stage I. The gas expands isothermally from A to B at temperature T_2. Heat is absorbed equal in amount to the work done by the system on the surroundings, since, for an ideal gas, the change in internal energy is zero.

$$q_2 = w_1 = RT_2 ln \frac{V_2}{V_1}.$$

Stage II. The gas expands adiabatically from B to C. The heat absorbed is zero; hence the work done is

$$w_2 = C_v(T_2 - T_1),$$

where $T_2 - T_1$ is the change in temperature resulting from the adiabatic expansion.

Stage III. The gas is compressed isothermally from C to D in a reservoir at T_1, whereby the heat q_1 is given up to the surroundings in amount equal to the work of compression

$$q_1 = w_3 = RT_1 ln \frac{V_3}{V_4}.$$

Stage IV. The gas is compressed adiabatically from D to A. The work done on the gas is

$$w_4 = C_v(T_2 - T_1),$$

where $T_2 - T_1$ is the increase in temperature produced by the adiabatic compression.

The net heat absorbed by the gas in the whole cycle is, therefore,

$$q = q_2 - q_1 = RT_2 ln \frac{V_2}{V_1} - RT_1 ln \frac{V_3}{V_4}.$$

From our knowledge of adiabatic expansions of an ideal gas we know that in the two adiabatic processes considered

$$C_v ln \frac{T_2}{T_1} = R ln \frac{V_3}{V_2} \quad \text{(Stage II)}$$

and

$$C_v ln \frac{T_2}{T_1} = R ln \frac{V_4}{V_1} \quad \text{(Stage IV)}.$$

Hence

$$\frac{V_3}{V_2} = \frac{V_4}{V_1} \qquad \text{or} \qquad \frac{V_2}{V_1} = \frac{V_3}{V_4}.$$

Hence

$$q = q_2 - q_1 = R(T_2 - T_1) ln \frac{V_2}{V_1}.$$

Similarly, the work done by the gas,

$$w = w_1 + w_2 - w_3 - w_4 = R(T_2 - T_1)ln\frac{V_2}{V_1},$$

which satisfies the condition for a cyclic process

$$w = q.$$

The work done may now be compared with the quantity of heat q_2 absorbed at the higher temperature T_2.

$$w = R(T_2 - T_1)ln\frac{V_2}{V_1},$$

$$q_2 = RT_2ln\frac{V_2}{V_1}.$$

Hence

$$w = q_2\frac{T_2 - T_1}{T_2}.$$

It is therefore evident that, in the cycle, a quantity of heat q_2 has been absorbed from the surroundings at a temperature T_2 and partly transformed into the work w, the remainder q_1 being given up to the surroundings when at a lower temperature T_1. The work obtained in such a process is a definite fraction, $(T_2 - T_1)/T_2$, of the absorbed heat. We may now proceed to an examination of the question whether this quantity of work w represents the maximum amount of work possible in such a heat transfer; whether also the same fraction would be obtainable were the system employed not an ideal gas. The answer to such problems leads us into the realm of the direction of energy change and the restrictions upon the interconvertibility of energy which experience has embodied in the second law of energetics.

The Second Law of Energetics

An inquiry into the direction of change which a given system will undergo may well be begun with an inquiry into some well-known examples of direction of change and the characteristics which such processes possess.

Reversible and Irreversible Processes: We are quite familiar with a variety of processes, both physical and chemical, which will proceed of themselves, or as we so designate them, spontaneously occurring processes. Heat is spontaneously transferred from a hot to a cold body either by contact or by radiation. Uniformity of temperature throughout the system will eventually result. With a concentrated solution in contact with a more dilute solution, diffusion of the solute will spontaneously occur and continue until a uniform concentration results. Gases permeate a vacuum. Similarly, the inter-diffusion of two gases when brought together is another familiar phenomenon. An electric current will flow along a conductor when differences of potential

manifest themselves, just as water will flow from a region of higher level to a lower level until a uniform level is secured throughout the system. Many chemical reactions occur spontaneously; ammonia and hydrogen chloride gas at ordinary temperatures when brought into contact will react to yield solid ammonium chloride. All such processes proceed of themselves; *they are also, of themselves, irreversible.* All are tending to a state of greater stability. The *velocity* with which such a position of greater stability is approached may vary widely. The *trend* in that direction is definite and cannot be reversed by the system of itself. Only by the employment of external agencies can the direction of such processes be reversed. The final state which such a system attains is spoken of as a state of equilibrium. A system in such a state is characterized by the uniformity in the intensity of all its forms of energy. In reaching this finality many halting places may occur. The system in such case is in a state of metastable equilibrium. Thus, for example, hydrogen and oxygen at room temperatures are only apparently in equilibrium. In reality they are in partial or metastable equilibrium, as the introduction of a small amount of platinum black into the system would demonstrate. Water would result from the interaction of the gases. But, in no conceivable manner, without the intervention of external agencies, could the process be expected to reverse itself, to proceed from the water stage back to the state of the gas mixture. We might generalize such observations in the conclusion that: *spontaneously occurring processes are irreversible.*

Let us now examine the conditions under which we must operate in order to approximate to reversibility in the conduct of a process. The direction which any energy change takes is determined by the relative magnitudes of the intensity factors of the energy of the system and of its surroundings. At equilibrium the intensities of all the forms of energy are uniform. An infinitesimal variation in any one intensity factor will produce a change in that direction which will tend towards uniformity.

Imagine a pure liquid in equilibrium with its saturated vapor enclosed in a cylinder fitted with a piston the pressure upon which may be delicately adjusted. Let the apparatus be at constant temperature in a large reservoir from which the system may withdraw heat or to which it may give up heat. The piston will be stationary when the pressure on the piston is exactly equal to the pressure of the saturated vapor at the given temperature. Any displacement of the pressure on the piston, no matter how small, will cause a change to take place in the system, liquid-vapor. If the pressure on the piston be diminished infinitesimally, the piston will rise. The volume occupied by the saturated vapor will increase and hence a little of the liquid will evaporate to produce the saturation pressure. In doing this, heat will be abstracted from the reservoir. In this way, a process may be continuously operated, namely, the change from liquid to saturated vapor at a given temperature. The process will be exceedingly slow since the difference in the intensity factors is, under assumption, infinitesimally small. The process may also be reversed. Imagine a pressure on the piston infinitesimally greater than the saturated vapor

pressure. The piston will, under such circumstances, compress the saturated vapor into a smaller volume, the supersaturation of the vapor which would thereby result being overcome by condensation of some of the vapor. By this reversal of the process vapor may be converted to liquid. Heat will be given up to the surrounding reservoir.

The energy expended in two such processes as we have just outlined may now be computed. Let the saturated vapor pressure at the constant temperature T be equal to p. In the first case let the pressure on the piston be $p - dp$, infinitesimally smaller than p. Let the volume change, dv, be infinitesimally small. The work expended by the system on the surroundings will be

$$(p - dp)dv = pdv - dp\,.\,dv.$$

If dp and dv are infinitesimally small, the second factor $dp\,.\,dv$ is an infinitesimal of the second order, negligible in comparison with $p\,.\,dv$. Substantially therefore, the work done is $p\,.\,dv$. In the second process considered, that of compression, the pressure on the piston must be slightly greater than p, say $p + dp$. Let the system, after the expansion, be compressed by such a pressure through a volume decrease $- dv$. The work done on the system will be

$$-(p + dp)dv = -(pdv + dp\,.\,dv)$$

or $- p\,.\,dv$ when second order infinitesimals are neglected. The system is now in its original condition, the heat changes paralleling the two processes having occurred and being demonstrably equal and opposite, provided that no accidental and irreversible processes have simultaneously occurred. For this, it is necessary to assume that the piston shall be both weightless and frictionless since otherwise irreversible changes, e.g., those due to friction, would doubtless have occurred. Such a process represents an ideal to which all naturally occurring processes may approximate without ever realizing. Such an ideal process, however, though not actually realizable, is, nevertheless, conceivable. From the mental conception and its consequences, definite conclusions may be reached. Such an ideal process is characterized by its complete reversibility in contrast to actual processes which will always contain elements of irreversibility to a greater or less degree. In the ideal process, all of the stages of the process may be repeated in inverse order in point of time, the net expenditure of energy by all the mechanical forces involved being zero on completion of the whole process.

One other example, involving another form of energy, may be cited to illustrate the concept of reversible processes and to show the approximation to the ideal process which may be achieved by a real process. The lead storage battery, when discharging, yields current at approximately 2 volts. When discharged the process may be reversed by supplying current to the battery. As normally operated, the process of discharge and charge is accompanied by a number of irreversible phenomena, diffusion of electrolyte, heat losses and the like. The discharge of the battery may, however, be secured under conditions approximating to the ideal reversible process by opposing to the flow of

current from the battery a current at a potential infinitesimally smaller than that of the battery. Under such circumstances current would be drawn from the battery in infinitesimally small amounts at minute speed and the factors of irreversibility in the process would be reduced to a minimum. At any moment by increasing the opposing potential infinitesimally beyond that of the battery the direction of current flow would be reversed, the battery would begin to charge. Furthermore, as in the previous case, the energy expenditure for any infinitesimal change in one direction will be exactly equal numerically to that expended in the reverse case. This type of reversible process is approximately obtained in the Poggendorf method of measurement of the electromotive forces of galvanic elements. The unknown potential is measured by opposing to it a potential of known magnitude, equality of potential being indicated by zero displacement of a galvanometer suitably placed in the electrical circuit. With such a system, very minute quantities of current could be drawn from a galvanic element and the actual conditions of energy change would approximate very closely to the ideal reversible conditions.

Maximum Work: It is characteristic of such ideal reversible processes that the external work performed by the system undergoing change is the maximum amount of work that the system is capable of accomplishing. It is very evident that, if all irreversible effects could be eliminated from a process, the efficiency of the process should be a maximum. This is actually true. It may be made the more evident from a reconsideration of some ideal processes. In the isothermal expansion of an ideal gas through an infinitesimal volume change, dv, the work done is pdv. The magnitude of this quantity is obviously dependent on the opposing pressure p. When p is zero, expansion against a vacuum, the work done is zero. As p is increased the work done, pdv, also increases. The value attains a maximum when the driving pressure of the gas is infinitesimally greater than the opposing pressure. For, if these two pressures are equal, no volume change can occur; and if the opposing pressure be infinitesimally greater than the gas pressure, contraction in volume of the system will result. The maximum external work is therefore done when driving and opposing forces differ infinitesimally. This condition is, we have seen, that demanded by an ideal reversible process at all stages of its operation. The external work performed in a reversible process is therefore the maximum work available in the conduct of the process. In the expansion process just discussed, the maximum work, A, done by the system is therefore

$$A = pdv.$$

For a finite volume change conducted isothermally and reversibly

$$A = \int_{v_1}^{v_2} pdv,$$

which, as we have previously shown for an ideal gas, is

$$A = RTln\frac{v_2}{v_1} = RTln\frac{p_1}{p_2}.$$

A little consideration will show also that the work done on the surroundings in an adiabatic expansion

$$C_v(T_1 - T_2) = \int_{v_1}^{v_2} p dv$$

also gives the maximum work available from the process. We may therefore conclude that in the complete cyclic process already considered, the Carnot Cycle, all the operations being conducted reversibly, the external work performed is the maximum work that can be accomplished in that cycle of operations. The relationship given by the Carnot Cycle may therefore be written

$$A = q_2 \frac{T_2 - T_1}{T_2},$$

the work done by the system in the transfer of heat q_2 from temperature T_2 to T_1 representing the maximum amount of work obtainable in an ideally conducted process. All real processes would yield a smaller amount of external work.

Furthermore, in a process consisting of a transfer of heat it may be shown that the fraction converted into useful work is independent of the mechanism whereby heat is transferred, provided that this mechanism is reversible. For, let us assume such a mechanism producing an amount of work w' greater than w obtained in the Carnot Cycle previously considered. In such case a quantity of heat, q_2, will be taken from the reservoir at T_2 and a quantity of heat q_1' ($<q_1$) be given to the reservoir at T_1, whereby the relationship is obtained,

$$q_2 - q_1' = w'.$$

Then, by employing the Carnot Cycle for an ideal gas, in the reverse direction from that previously considered, a quantity of heat q_1 can be taken from the reservoir at T_1 and with the aid of a portion of the work w', actually the quantity w,an amount of heat q_2 can be put back into the reservoir at temperature T_2. As a result of this compound cycle the only change in the system as a whole is tha t a quantity of heat $q_1 - q_1'$ has been taken from a reservoir at T_1 and converted into useful work, $w' - w$, without causing any other permanent changes in the system as a whole. Experience teaches that such a machine is impossible. It is not in contradiction of the First Law of Energetics, since heat energy is consumed in the production of work. But the possibility of constructing such a machine is denied by the Second Law of Energetics, based upon the experience of man in the search for such a machine. Were such a machine possible, whereby heat could be continuously converted into work without compensation, an even more wonderful perpetual motion than that denied by the First Law would be possible. It would be possible continuously to utilize the large heat reservoirs of our environment to supply the motive power of our universe. It would be possible, for example, to drive a ship with the store of heat energy available in the ocean in which the ship was

placed. Such a perpetual motion machine, which Ostwald has called a perpetual motion machine of the second kind, is specifically denied by experience and has resulted in the enunciation of the second law of energetics. For useful work to be produced from heat without compensation, a transfer of heat from a higher to a lower temperature is demanded. The fraction of heat converted into work is given by the equation

$$w = q_2 \frac{T_2 - T_1}{T_2},$$

and this is the maximum work available. It is therefore evident that whatever the reversible mechanism used for the heat transfer from a higher to a lower temperature reservoir the maximum work available is a constant.

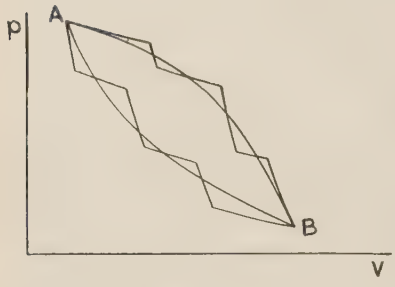

Fig. 3

With an engine working in a heat reservoir at its own temperature it is obvious that $T_2 - T_1$ and, therefore, A must be zero. It follows also that the work done in an isothermal reversible cycle is equal to zero, since the internal energy does not change, $\Delta U = 0$, and, by the second Law, the heat of the isothermal environment cannot be converted into useful work.

Any reversible cycle can be shown to be equivalent to a sum of Carnot cycles. In the accompanying diagram, Fig. 3, let the continuous lines AB, BA represent the path of a reversible cycle. It is evident that the path A to B may be traversed by a number of isothermals and adiabatics as shown. Similarly the return path may be so traversed. The broken line path A to B approximates the more closely to the continuous curve AB the more minute the isothermal and adiabatic changes become. The same holds true for the reverse path BA. By prolonging the isothermals back into the enclosed portion of the diagram it is evident that the area ABA may be regarded as made up of a large number of infinitely small Carnot cycles actually equal to the reversible cycle under consideration. In the summation, all those portions of the small isothermals within the actual cycle will be traversed once in the one direction, once in the reverse direction so that the net resultant of such sections is zero. The properties of any reversible cycle will therefore be equal to the summation of the properties of all the Carnot cycles of which it may be regarded as composed.

The maximum work which a given process is capable of accomplishing is a fixed and definite quantity characteristic of the process, determined solely by the initial and final states of the system independent of the path between. Were this not so it is immediately evident that a perpetual motion machine could be constructed whereby in the process

$$X \rightarrow Y$$

a reversible path could be selected in which the maximum work, A, done by the system on the surroundings in the passage from X to Y was numerically greater than A', the maximum work consumed by the system in the return from Y to X by a different reversible path. The system would now have completed a cycle and a quantity of work $A - A'$ would have been made available. The process could be repeated indefinitely. Such a production of energy whether created or produced at the expense of the thermal environment is denied by the two laws of energetics which have been discussed. Hence, it must follow that $A = A'$. Since these were the maximum work quantities for any two possible methods of conducting the process, it follows that, for any path, the maximum work must always be a constant quantity. The maximum work done is therefore analogous to ΔU, the change in internal energy of the system, in that it is a function of the initial and final states and independent of the path. We may therefore define maximum work by means of the equation

$$\Delta A = A_B - A_A$$

in which the maximum work performed is the difference of two magnitudes' A_A and A_B which characterize the maximum work contents of the system in its initial and final states A and B. It is evident that, with this latter convention, the A of the preceding discussion is equal to $-\Delta A$.

The Concept of Entropy: In the discussion of the Carnot Cycle and in the generalization of the conclusions therefrom for any reversible cycle, we saw that the heat q_2 taken isothermally from a reservoir at T_2 was related to the heat q_1 given up to the reservoir at T_1 and to the maximum work A by means of the relation

$$q_2 - q_1 = w = A = \frac{T_2 - T_1}{T_2} q_2.$$

It follows, therefore, for any reversible cycle, that

$$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

or that

$$\frac{q_1}{T_1} = \frac{q_2}{T_2}.$$

If the cycle is not reversible, if any irreversible effects are present resulting in the dissipation of heat, it is evident that the work done, w, must be less than $[(T_2 - T_1)/T_2]\, q_2$. Under such circumstances

$$\frac{q_2 - q_1}{q_2} < \frac{T_2 - T_1}{T_2}$$

or

$$\frac{q_2}{T_2} < \frac{q_1}{T_1}.$$

Regarded from the standpoint of the machine conducting the Carnot Cycle the above expression for the equality of q_1/T_1 and of q_2/T_2 may be rearranged so that $+ q$ represents heat absorbed by the machine. In such circumstance we have for the Carnot Cycle

$$\frac{(-q_1)}{T_1} = \frac{(q_2)}{T_2}$$

or

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0.$$

Similarly for an irreversible process

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} < 0,$$

where again q_1 and q_2 are the heats *absorbed by the machine* at the two temperatures.

For each individual Carnot Cycle into which a reversible cycle may be divided, the relationship

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0$$

will hold. When the isothermal and adiabatic changes of each Carnot Cycle are infinitesimally small, the summation of the Carnot cycles is equal to the reversible cycle ABA in the preceding diagram. For the Carnot cycles we therefore have

$$\sum \frac{q}{T} = 0$$

and when the changes are infinitesimal we have correspondingly

$$\int \frac{dq}{T} = 0,$$

an expression which is therefore applicable to any reversible cycle irrespective of its nature or the path by which it is achieved provided that this be a reversible path. In the preceding figure, where the cycle is achieved in two stages A to B and B to A, it is evident that

$$\int \frac{dq}{T} = \int_A^B \frac{dq}{T} + \int_B^A \frac{dq}{T} = 0.$$

Both of these integrals are evidently independent of the path taken from A to B or conversely from B to A. Both are therefore determined by the properties of the initial and final states A and B. They are therefore evidently equal to the change in some single-valued function of the variables of the states A and B of the system. Let us express this by the relationship

$$\Delta S = S_B - S_A = \int_A^B \frac{dq}{T},$$

whence it follows that

$$dS = \frac{dq}{T}.$$

These expressions give us a definition of the entropy of a system. The increase ΔS in the entropy, S, of a reversible process is the integral of all the heat changes which the system undergoes in passing from state A to state B, each heat change to be divided by the absolute temperature at which it occurred. The concept of entropy received this definition from Clausius who emphasized its importance in the formulation of the statement of the second law of energetics, its dependence on the state of the system and its independence of the path by which the state is achieved.

It may also be demonstrated that the entropy of an isolated system is the sum of the entropies of the component elements of the system. Let us assume a system in which the component elements have internal energies respectively U_A, U_B, $U_C \cdots$, pressures p_A, p_B, $p_C \cdots$, volumes v_A, v_B, $v_C \cdots$ and entropies S_A, S_B, $S_C \cdots$, the whole system at a common temperature T. Let us assume for simplicity that external work changes in the system only involve mechanical energy. For any infinitesimal change occurring in the system, for example, to the component A, we have

$$q_A = dU_A + p_A dv_A.$$

The corresponding entropy change will be

$$dS_A = \frac{q_A}{T} = \frac{dU_A + p_A dv_A}{T}.$$

Similar equations hold for other changes in the system. Since the system is assumed isolated,

$$dq_A + dq_B + dq_C + \cdots = 0.$$

Hence

$$dS_A + dS_B + dS_C + \cdots = \frac{dq_A + dq_B + dq_C + \cdots}{T} = 0.$$

Or alternatively,

$$d(S_A + S_B + S_C + \cdots) = 0.$$

In other words, the entropy of an isolated system remains unchanged. Consequently the change of entropy in an adiabatic process is therefore zero. Also the entropy of the system is equal to the sum of the entropies of the component parts of the system.

Entropy Change in an Ideal Gas: For an ideal gas the heat absorbed in any process of change

$$q = \Delta U + p\Delta v.$$

For an infinitesimal change,

$$dq = dU + pdv.$$

Hence

$$dS = \frac{dq}{T} = \frac{dU + pdv}{T} = \frac{C_v dT + pdv}{T}.$$

If we assume that C_v is independent of temperature,

$$S = \int dS = C_v \int \frac{dT}{T} + R \int \frac{dv}{v} + \text{constant}$$
$$= C_v ln T + R ln v + \text{constant}.$$

For a definite volume change, for example, an isothermal compression from v_A to v_B of one mol. of gas

$$S_B - S_A = R ln \frac{v_B}{v_A}.$$

Since v_B is less than v_A, it is evident that the entropy of an ideal gas decreases during an isothermal compression. Conversely, in an isothermal expansion, the entropy of the gas increases by an amount equal to $R ln(v_B/v_A)$, where v_B is now greater than v_A.

Entropy Change in Irreversible Processes: The transfer of heat from a hotter to a colder system constitutes a simple irreversible process. Let us imagine an isolated system consisting of two reservoirs at temperatures T_2 and T_1 ($T_2 > T_1$) and a machine, e.g., an ideal gas, by which heat may be transferred. By allowing the gas to expand isothermally in the reservoir of heat at T_2, an amount of heat q may be taken from the reservoir. The gas may now be allowed to expand adiabatically until a temperature T_1 is attained. By placing the gas in contact with reservoir at T_1 and isothermally compressing, an amount of heat, q, may be communicated to the reservoir at T_1. The change in entropy of the gas is

$$\frac{q}{T_2} - \frac{q}{T_1}.$$

The change in entropy of the reservoirs considered as a system is equal to

$$-\frac{q}{T_2} + \frac{q}{T_1} = \frac{q}{T_1} - \frac{q}{T_2}.$$

Now, since T_2 is greater than T_1, we conclude that the conduction of heat from a reservoir of high temperature to one of low temperature results in an increase of entropy of the reservoir system.

The expansion of an ideal gas from volume v_A to volume v_B against a vacuum is another irreversible process, in which, as already shown,

$$S_B - S_A = R ln \frac{v_B}{v_A},$$

in which therefore an entropy increase of the gaseous system results.

We may therefore generalize our conclusions with regard to entropy change in the following manner. In irreversible processes, the entropy of all the systems involved in the change is increased. In ideal reversible processes, the entropy of the system as a whole is unchanged. The change in entropy of any portion of such a system undergoing a reversible change is equal to the heat which such portion of the system absorbs divided by the absolute temperature at which the heat is absorbed.

Now since all real processes are irreversible, we have a method of statement of the Second Law of Energetics. It may be thus expressed: *All naturally occurring processes are accompanied by an increase in the entropy of the system.* The content of the two laws of energetics may be summed up in the aphorism of Clausius: "The energy of the universe is constant; the entropy of the universe tends towards a maximum." This formulation of the second law provides us with one criterion of the direction of change which a given system will take if allowed to change spontaneously. The change will occur in that direction in which an increase in the entropy of the system is obtained.

Free Energy: We may now proceed to an examination of other thermodynamic magnitudes which have proved useful in the problems raised by the Second Law of Energetics, which will have, moreover, a greater applicability to problems of chemical change than the broader concept of entropy. Only at a later stage, when the theorem of Nernst, sometimes termed the Third Law of Thermodynamics, has received a detailed treatment, will the concept of entropy be applied in its most useful form.

For a reversible process we have seen that the entropy of an isolated system, machine plus surroundings, remains constant.

$$\Delta S = 0.$$

Let us define two quantities by the equations

$$A = U - TS$$

and

$$F = H - TS = (U + pv) - TS = A + pv.$$

For any given isothermal change we can derive corresponding equations as, for example,

$$\Delta A = \Delta U - T\Delta S.$$

If this equation apply to any reversible change at temperature T, it follows from the preceding section that $T\Delta S$ is equal to q, the heat absorbed in the process. Hence, from the equation for the first law,

$$\Delta U = q - w,$$

it follows that

$$\Delta A = -w$$

or alternatively that $-\Delta A$ is equal to the total work done by the system on the surroundings and, since the process in question is assumed to be reversible,

it represents the maximum work which the system is capable of accomplishing. It is, in other words, identical with the quantity which we have designated by the term A in the earlier sections.

In a process at constant temperature and constant pressure it is obvious that the work done by the system will be composite of two factors, that involved in the volume change, namely, $p\Delta v$ and a residual quantity w' which may be one of many energy quantities. A frequent form of such energy obtained in the conduct of chemical processes is electrical energy. Radiant energy, in the form of light, may be produced. Similarly, other forms are possible. In such case $w' + p\Delta v = w$. The quantity $p \,.\Delta v$ is constant irrespective of the mode of conduct of the process. The magnitude of the quantity w' will vary with the mode of conduct of the process. The greater the degree of irreversibility in the process, the less will w' be. It is conceivable that it may be zero, indicating complete irreversibility. The more the process approximates to reversible conditions, that is, the more w approximates to its maximum value, the greater will w' become. With a completely reversible isothermal process at constant pressure

$$w' + p\Delta v = w = -\Delta A.$$

Hence

$$w' = -\Delta A - p\Delta v.$$

Whence, from the equation $F = H - TS = A + pv$,

$$w' = -\Delta F = F_A - F_B.$$

These two quantities $-\Delta A$, the "Free Energy" of Helmholtz, and $-\Delta F$, the "Thermodynamic Potential" of Gibbs, are, as will be shown, of extraordinary utility in dealing with processes of chemical change. It is apparent that the quantity $-\Delta A$ is of importance when the variables chosen are volume and temperature. For pressure and temperature as chief variables the quantity ΔF has the preference; this will be generally true since constant temperature or constant pressure normally prevail in most chemical experiments. For reaction at constant volume and pressure it is evident that

$$\Delta A = \Delta F.$$

From the equation

$$F = H - TS$$

we obtain by differentiation with respect to pressure

$$\left(\frac{\partial F}{\partial p}\right)_T = \left(\frac{\partial H}{\partial p}\right)_T - T\left(\frac{\partial S}{\partial p}\right)_T.$$

Now

$$H = U + pv$$

or

$$dH = dU + pdv + vdp = TdS + vdp.$$

Hence

$$v = \left(\frac{\partial H}{\partial p}\right)_T - T\left(\frac{\partial S}{\partial p}\right)_T.$$

Hence also

$$\left(\frac{\partial F}{\partial p}\right)_T = v.$$

Or, for an isothermal process,

$$\int dF = \int v dp.$$

Similarly, the variation of F with temperature may be ascertained. Thus,

$$F = H - TS.$$

Hence

$$\left(\frac{\partial F}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p - T\left(\frac{\partial S}{\partial T}\right)_p - S.$$

Now

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p \qquad \text{and} \qquad T\left(\frac{\partial S}{\partial T}\right)_p = C_p.$$

Hence

$$\left(\frac{\partial F}{\partial T}\right)_p = -S = \frac{F - H}{T},$$

or

$$F - H = T\left(\frac{\partial F}{\partial T}\right)_p.$$

Correspondingly for a change in the quantity F in an isothermal process of change from state A to state B we may write this equation in the form

$$\left(\frac{\partial(\Delta F)}{\partial T}\right)_p = \frac{\Delta F - \Delta H}{T}$$

or

$$\Delta F - \Delta H = T\left(\frac{\partial(\Delta F)}{\partial T}\right)_p.$$

This equation enables us to calculate the change in thermodynamic potential of a reaction at any temperature when it is known at any given temperature. For a reaction at constant volume the corresponding equation will be

$$\Delta A - \Delta U = T\left(\frac{\partial(\Delta A)}{\partial T}\right)_v.$$

Applied to reversible galvanic cells these equations give us the well-known Gibbs-Helmholtz equation. For a reversible cell having an electromotive force E at constant temperature T and a temperature coefficient dE/dT it is evident that, when operated at constant pressure p,

$$-\Delta F = nFE,$$

where nF is the number of coulombs of electricity yielded by the cell when operated under such circumstances that the maximum electrical work is accomplished. Hence therefore,

$$-nFE - \Delta H = -nFT\frac{dE}{dT}$$

or

$$nFE + \Delta H = nFT\frac{dE}{dT}.$$

Thermodynamic Equilibrium: A condition of equilibrium may be defined by stating that a system is in equilibrium when it shows no change of state in any particular with time. The system must be in a state of absolute rest. A state of partial equilibrium is familiar to every one. A mixture of hydrogen and oxygen at room temperatures is one such example already discussed in an earlier section.

A state of absolute rest is difficult to determine experimentally. This fact may be illustrated by the case of the mixture of hydrogen and oxygen just cited. If, for example, such a gas mixture were stored over mercury at room temperature, no change in volume would be noted over long periods of time. This does not mean, however, that no chemical change is occurring. Let it be assumed that 10^6 molecules of hydrogen and half this number of oxygen molecules are reacting *per second.* A simple calculation, employing for the Avogadro number, $N = 6.06 \times 10^{23}$ moleculus per gram molecule, will reveal that it would require a period of observation extending over 2×10^6 years before a volume contraction of 1 cc. could be observed. It is very evident, therefore, that any thermodynamic criteria for a state of absolute rest or of chemical equilibrium would be extremely valuable if not absolutely necessary.

We saw that it was characteristic of reversible processes that the smallest change in any of the intensity factors of the various energy quantities obtaining in the system was sufficient to cause a displacement of the system in one or other direction dependent on the sign of the change in the intensity factor. The same is true for any system in thermal equilibrium. Every infinitesimal change in such a system is reversible. We have seen that the criterion of this reversibility is that

$$dS = 0.$$

Now

$$F = H - TS$$

or

$$= U + pv - TS.$$

Hence, by differentiation,

$$dF = dU - TdS - SdT + pdv + vdp.$$

For reversible processes

$$dU - TdS = -pdv.$$

Hence

$$dF = -SdT + vdp.$$

It therefore follows that, for reversible changes at constant temperature and constant pressure,

$$dF = 0.$$

This expression becomes, therefore, a second criterion for equilibrium conditions. A system is in equilibrium when a small displacement in the conditions of the system can be accomplished without change in the thermodynamic potential.

For a system which is not in equilibrium the direction of change may also be stated. Any naturally occurring process results in an increase in the entropy of the system as a whole. Now, since

$$\Delta F = \Delta H - T\Delta S,$$

it is evident that $T\Delta S$ must always be positive in spontaneously occurring processes. If the system be isolated, it is clear that ΔH is zero. Hence ΔF must be negative in all such processes. We therefore conclude that the thermodynamic potential of all spontaneously occurring processes decreases. It will be shown in the sequel how important is this criterion of the direction of chemical change.

Some writers have assigned to this concept of thermodynamic potential the term "free energy" originally used by Helmholtz to designate the function A which we have considered above. It is evident that the thermodynamic potential is in reality the free energy change accompanying an isobaric process. In succeeding chapters the term free energy is used to denote F, in agreement with recent practice among physical chemists in America.

The magnitude of the free energy decrease accompanying a process is evidently a measure of the tendency of a system to react—a concept which from very earliest times has been designated as the chemical affinity of a system. The free energy decrease gives therefore a quantitative measure of the tendency of the system to undergo reaction. It is immediately evident that the information we possess concerning the magnitude of the free energy decrease is in accord with our ideas concerning affinity. If a system is in equilibrium, the chemical affinity is nil. This is in accord with our deduction that for systems in equilibrium $dF = 0$. The further removed a system is from its equilibrium state the greater the chemical affinity. Likewise the greater is the free energy decrease accompanying the change of such a system to equilibrium conditions.

Entropy Change with Volume and Pressure: We have seen that

$$TdS = dU + pdv.$$

For an isothermal process it follows, by differentiation with respect to volume that

$$p = T\left(\frac{\partial S}{\partial v}\right)_T - \left(\frac{\partial U}{\partial v}\right)_T.$$

If we further differentiate this expression with respect to temperature, the volume being assumed constant we obtain

$$\left(\frac{\partial p}{\partial T}\right)_v = T\frac{\partial^2 S}{dTdv} + \left(\frac{\partial S}{dv}\right)_T - \frac{\partial^2 U}{\partial T \partial v}.$$

Now since, at constant volume,

$$dS = C_v \frac{dT}{T},$$

it follows that

$$\left(\frac{\partial S}{\partial T}\right)_v = \frac{C_v}{T} \qquad \text{and} \qquad \frac{\partial^2 S}{\partial v \partial T} = \frac{1}{T}\left(\frac{\partial C_v}{\partial v}\right)_T.$$

Also

$$\frac{1}{T}\left(\frac{\partial^2 U}{\partial T \partial v}\right) = \frac{1}{T}\left(\frac{\partial C_v}{dv}\right)_T,$$

since

$$\left(\frac{\partial U}{\partial T}\right)_v = C_v.$$

Hence we derive the expression

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial S}{\partial v}\right)_T$$

which is the desired variation of entropy with volume.

Similarly, with respect to the variation of entropy with pressure, since

$$H = U + pv, \qquad dH = dU + pdv + vdp = TdS + vdp.$$

Hence

$$v = -T\left(\frac{\partial S}{\partial p}\right)_T + \left(\frac{\partial H}{\partial p}\right)_T.$$

By differentiating further with respect to temperature and again eliminating identities we obtain

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p.$$

It will be noted that these are general expressions applicable alike to all states of matter and, indeed, to equilibria involving one or more phases of matter.

The Clapeyron-Clausius Equation: We may utilize such expressions in the important problem of the variation in the equilibrium vapor pressure of a system with variation in temperature. As we have just seen,

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial S}{\partial v}\right)_T.$$

In respect to the process of vaporization, the pressure p is independent of the

volume. Furthermore, we may replace the infinitesimal dS/dv by the expression $\Delta S/\Delta v$ which refer to one mol of the substance in question. Hence, for the vaporization of any substance

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta v}.$$

We know also that for any system in equilibrium

$$\Delta S = \frac{\Delta H}{T}.$$

Our expression therefore becomes

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta v}.$$

In this equation ΔH is actually the latent heat of vaporization λ of the substance so that we obtain

$$\frac{dp}{dT} = \frac{\lambda}{T\Delta v}.$$

This expression, which is quite generally applicable, can be transformed into a familiar form when applied to vapors sufficiently dilute that the equation $pv = RT$ can be assumed to hold and the volume of the vapor is large compared with that of the condensed system. In such case the equation becomes

$$\frac{dp}{dT} = \frac{\lambda}{T(V_g - v_l)}$$

or

$$\frac{dp}{dT} = \frac{\lambda}{T \cdot \dfrac{RT}{p}}$$

or

$$\frac{dp/p}{dT} = \frac{\lambda}{RT^2}$$

or

$$\frac{d\ln p}{dT} = \frac{\lambda}{RT^2}$$

Entropy Change Accompanying Fusion and Vaporisation: At the freezing point and boiling points, these processes of fusion and vaporization are respectively equilibrium processes. With pure substances the temperature is constant. In each case therefore

$$T \cdot \Delta S = \Delta H,$$

where ΔH is the latent heat of fusion or vaporization and T is the absolute temperature of the fusion or vaporization.

Entropy Change with Temperature: We have already pointed out that

$$\left(\frac{\partial S}{\partial T}\right)_v = \frac{C_v}{T} \qquad \text{and} \qquad \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}.$$

It follows therefore that the entropy change upon change of temperature from T_1 to T_2 at constant pressure is given by the expression

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T}\, dT = \int_{T_1}^{T_2} C_p d\ln T.$$

To evaluate such an integral it is therefore necessary to know the variation of heat capacity with temperature. This known, the integral may be solved either from an equation in powers of T expressing such variation or, alternatively, by graphical methods.

In the succeeding chapters of the book, the many applications of the fundamental concepts herein detailed will be brought forward. It will emerge that the thermodynamic method constitutes a most effective auxiliary of the atomistic or kinetic method of treatment, the one confirming and in some cases amplifying the conclusions deduced by the aid of the other.

CHAPTER III[1]

THE KINETIC THEORY OF GASES AND LIQUIDS

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The following symbols are used in Chapters III and IV of this book:

a, b } van der Waals' constants
c concentration (mols/cc)
d diameter
e base nat. log.
f function, accommodation coeff.
g acceleration of gravity
i index
j chemical constant
k Boltzmann const.
l length
m mass of molecule
n number of mols.
p pressure
r radius
s index
t degrees Centigrade; time
u energy of N molecules
v arbitrary volume
w molecular velocity
x, y, z } position coördinates
$\overline{m}$ relative mass

A area
B constant
I moment of inertia
K equilibrium constant
M molecular weight
N number of molecules in vol. v
Q heat of reaction per mol.
R radius, gas constant per mol.
S entropy per mol.
T °K.
U energy per mol
V mol. volume
W bulk velocity
X, Y, Z } coörd. axes
N_A = Avogadro number per mol
$\mathfrak{N}$ = number of collisions
N = number of molecules/cc.
α constants
β "
δ thickness
ϵ energy per molecule (ϵ_p = potential energy)
η viscosity
ϑ colatitude
λ thermal conductivity
ν frequency
π 3.14 . . . reduced pressure
ρ density (mass)
σ density of statepoints on surface of sphere
τ time, reduced temp.
υ reduced volume
ω solid angle; angular velocity; element of volume in velocity space
φ longitude
ξ, η, ζ } components of w
Δ difference
Λ mean free path
Π multiple product
Σ sum

[1] This chapter is an enlarged and revised translation of chapter I and parts of chapter III and chapter V of "Die kinetische Theorie der Wärme," by K. F. Herzfeld, Braunschweig F. Vieweg, 1925, which forms the second half of Volume III, Müller-Pouillets Lehrbuch der Physik, 11 ed.

A general outline of the atomic concept has been given in the first chapter. The usefulness of this concept is greatly increased if it is combined with the kinetic theory. Pure thermodynamics needs no particular theory about the nature of heat, apart from the results implied in the first law, that heat is some kind of energy. The kinetic theory of heat, however, asserts that this energy is not a new type, but is entirely made up of the " hidden " motions of the particles (atoms and molecules) and a potential energy of elastic or electric kind connected with deviations from equilibrium positions, deviations which are due to the motion mentioned above. The motions are " hidden," in general, only on account of the small size of the particles, together with the irregularity of the motion, in the same way in which a crowd of people moving irregularly in different directions (without preference) seems at rest if seen from far above. The importance of the irregularity of the motions together with the importance of the large number of individuals is thus evident at the outset. These two qualities will require a particular kind of mathematics, namely, the calculus of probability.

To explain, then, the general laws of thermodynamics, which apply to all substances, it is necessary to have a very general theory. This theory is treated in the subject of " statistical mechanics," but on account of its great generality it cannot give everything in detail. In the case of the simplest substances, the gases, however, it is possible for the kinetic theory to give all the details.

This theory employs a method which is as essential here as in the other branches of theoretical physics. That is, as large a part of the theory as possible is built up from a greatly simplified model. To give an example, it is known, as explained in the first chapter, that in reality a molecule is a very intricate structure of electrons and nuclei moving in a complicated manner. In the case of many characteristic features of the behavior of the molecule, as in a rather rough description of its motion as a whole, this internal structure plays no rôle. Accordingly, in describing this motion the internal structure is disregarded and the molecule is treated as a hard solid sphere. This implies that the internal structure of the molecule does not affect its behavior as a whole. When the molecules are close together (dense gas), however, the details of their surfaces, their mutual forces, etc., become important, and it is then necessary to replace the primitive picture with one closer to reality, but much more complicated.

The kinetic theory of gases endeavors, then, to explain the behavior of a gas, not only as far as it is prescribed by the general thermodynamical laws, but also in so far as it is peculiar to a gas, with the simplest possible assumptions.

Comparison of a gas with a crystal shows as the most marked difference, that, in the latter case, there are internal stresses resisting both tension and compression, so that the crystal takes on a definite shape and volume, if constraints are absent, while a gas resists compression, but fills voluntarily and completely a volume of any size. Accordingly, it is natural to assume that there are in a crystal forces which tend to keep the molecules in a position of

equilibrium, while in a gas at least the attractive forces are not sufficient to keep the molecules together. The simplest assumption, which will be made first, is that the forces between the gas molecules can be neglected entirely; the pressure exerted on the walls must then be explained as a kinetic effect, resulting from the impact of the gas molecules against this wall. The gas molecules move, according to this hypothesis, on the whole in straight lines (in the absence of an external force like gravity), occasionally broken by collisions among themselves or with the walls, during which collisions the molecules behave approximately like hard elastic spheres. The apparent uniformity of the gas density is only an average effect, due to the large number and swift irregular motion of the particles.

While a surprisingly correct theory of the forces in crystals was given as early as 1760 by Boscovich[1] and taken up in the elastic theories of Laplace, Navier, Poisson and Cauchy, the recognition that the gas pressure is entirely due to the dynamic effect of impacts took a long time. It is true that Bernoulli and Herapath[2] had expressed this opinion but one often finds, in papers from the first half of the XIX century, the expression "the elastic tension of gases." Waterstone in 1845 sent a paper to the Royal Society in which a large number of later developments were contained, but it was not deemed worthy of publication, and was only rediscovered and published by Lord Rayleigh in 1892. Following a new (1851) suggestion of Joule, the present theory of gases dates back to two papers by Krönig and Clausius.[3] Its brilliant development in the next 30 years is most closely connected with the names of Clausius, Maxwell and Boltzmann. Later contributions of importance will be found in the text.[4]

GASES IN EQUILIBRIUM

Gaseous Pressure; Boyle's Law: Fig. 1 shows a section of a rectangular box with sides of lengths l_1, l_2, and l_3. The box is fitted with a frictionless piston, A, which can move along the sides of length l_1. The walls of the box, together with the piston, are supposed to be perfectly smooth and elastic. The box contains a single molecule which is assumed to be a small, hard, perfectly elastic sphere. It is further assumed, for the present, that the

[1] Theoria philosophiae naturalis redacta ad unicam legem virium in natura existentium auctore Patre R. T. Boscovich, S. J. Venice, 1763.

[2] D. Bernoulli, Hydrodynamice (1738) Argentoratum (Ausburg); W. Herapath, *Phil. Mag.*, **62** (1823); **64** (1824).

[3] A. Krönig, *Pogg. Ann.*, **99**, 322 (1856); R. Clausius, *Pogg. Ann.*, **100**, 366 (1857).

[4] The classical and in many respects still unsurpassed textbooks on the Kinetic Theory of Gases are: L. Boltzmann, Vorlesungen uber Gas theorie, 2 vol., 1st ed., Leipzig 1896 and 1898, 3rd reprint 1920; J. H. Jeans, Dynamical Theory of Gases, Cambridge, 4th ed., 1925. Newer Books: L. Bloch, The Kinetic Theory of Gases, London 1924; L. B. Loeb, Kinetic Theory of Gases, New York, 1927; R. C. Tolman, Statistical Mechanics, New York 1927; G. Jäger, Kinetic Theory in Volume IX, Handbuch d. Physik, Berlin 1926. For the exposition of the logical foundations of the theory and of many defects in the usual proofs see: P. and T. Ehrenfest, Statistische Mechanik in Volume IV, 32, of Enzyklopadie d. Math. Wiss. Leipzig, 1911.

molecule moves exactly parallel to the l_1 edge as shown in Fig. 1. The influence of external forces such as gravity will be disregarded. Now the molecule will collide periodically with the piston and these impacts will set the piston in motion. To counteract this a force F, directed inward, is applied to the piston.

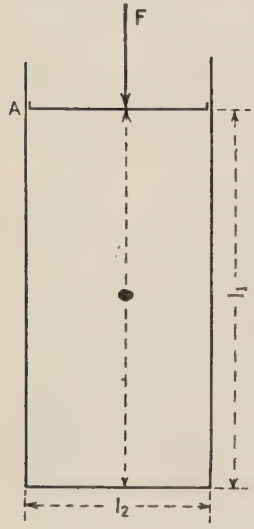

FIG. 1.

That the piston will not be absolutely stationary is evident from the fact that the applied force is acting during the intervals between collisions and is then moving the piston into the box. At the instant of collision the impact prevails and the piston is driven in the reverse direction. The applied force must be of such magnitude that the two displacements are equal and opposite. This is the case if the applied force equals the time average of the impulsive forces of collision, which is the momentum imparted per second by the molecule to the piston. F is then equal to the "pressure" exerted by the molecule times the area of the piston.

The change of momentum accompanying each collision will first be calculated. A molecule of mass m and velocity ξ has a momentum equal to $m\xi$. This is all imparted to the piston when the molecule is brought to a complete stop. Since however, both the piston and the molecule are perfectly elastic, they do not remain in contact,[1] but the molecule rebounds with its original speed. During this acceleration (which is similar to that experienced by a rubber ball when pressed against a hard plane and then released) a further momentum $m\xi$ is given to the piston. From each collision, therefore, the piston receives a momentum directed outward and equal to

$$2m\xi. \tag{1}$$

Since the distance between the piston and the opposite wall is l_1, the time between two successive collisions is

$$\frac{2l_1}{\xi}. \tag{2}$$

Hence the number of collisions the molecule makes with the piston in unit time is

$$\frac{\xi}{2l_1} \tag{3}$$

and the total momentum received by the piston in unit time is

$$2m\xi \cdot \frac{\xi}{2l_1} = \frac{m\xi^2}{l_1}, \tag{4}$$

which, at equilibrium, must be equal to the applied force.

[1] Actually they remain in contact for a short time, but this does not alter the result.

If, instead of a single molecule, there are N_1 molecules moving independently of each other but all exactly parallel to the l_1 edge, N_1 times as many collisions occur and the force is N_1 times as great. The pressure (force per unit area) which is acting on the piston is therefore

$$p_x = \frac{N_1 \frac{m\xi^2}{l_1}}{l_2 l_3} = \frac{N_1 m\xi^2}{l_1 l_2 l_3} = \frac{N_1 m\xi^2}{v}, \tag{5}$$

where $v = l_1 l_2 l_3$, the total volume of the box.

Since $N_1 m$ is the total mass of the gas (M_1) and $M_1\xi^2/2$ the kinetic energy of its molecules $\left(U_{1k}\frac{N_1}{N_A}\right)$

$$pv = 2U_{1k}\frac{N_1}{N_A}, \tag{6}$$

where U_{1k} is the kinetic energy of one mol of the molecules of type 1 and N_A is the Avogadro number per mol.

Actually the molecules do not move along exactly parallel paths [1] but, as will be seen in the following paragraphs, in all possible directions. This chaotic condition can be approximated by the assumption that one third of the total number of molecules N move up and down, one third from right to left, and one third backwards and forwards. Then

$$N_1 = \frac{N}{3}. \tag{7}$$

Then (6) takes the form [2]

$$pv = \tfrac{2}{3}U_k\frac{N}{N_A}. \tag{9}$$

$$\frac{N}{N_A}U_k = \frac{Nmw^2}{2}. \tag{10}$$

where U_k is now the kinetic energy of one mol. That is, only one third of the total kinetic energy contributes to the pressure against a given wall.

If there are different kinds of molecules present, as in a mixture of gases, the argument remains unaltered and there is obtained

$$pv = \frac{2}{3}\left(U_k'\frac{N_1}{N_A} + U_k''\frac{N_2}{N_A} + \cdots\right), \tag{11}$$

where

$$\frac{N_s}{N_A}U_k^{(s)} = \frac{N_s m_s w_s^2}{2} \tag{12}$$

is the total kinetic energy of all molecules of the s-th kind.

[1] Such an imaginary gas, all of whose molecules move parallel to each other is called a "one-dimensional gas." If the molecules are imagined to be moving in a plane, the result is a so-called two-dimensional gas.

[2] $$w^2 = \xi^2 + \eta^2 + \zeta^2 \tag{8}$$

(ξ, η and ζ are the components of the velocity, w, along the X, Y and Z axes respectively.)

Boyle's law is therefore a direct result of this assumption since the number of collisions in unit time, (and therefore the pressure) is proportional to the density (N/v) of the gas. In this discussion, it is assumed that the momentum imparted by each collision and hence the kinetic energy of the molecules is not dependent upon the volume, but upon other independent variables. This assumption will be proven on p. 83 ff.

Upon increasing the number of molecules the time between two successive impacts is naturally decreased, at the same time diminishing the oscillation of the piston. It will be shown later on that under ordinary conditions (atmospheric pressure and room temperature) there are from 10^{23} to 10^{24} collisions per second on each square centimeter of the wall. The duration of each collision must be regarded as at least of the order of magnitude of the time between two successive collisions and in this case the effect may be correctly considered as a continuous pressure. The smaller the surface or the number of molecules, the smaller will be the number of collisions and the larger the relative irregularities of the state.

The total pressure of a dilute gas is accordingly produced by the thermal motion of the molecules and is therefore known as a thermal pressure.

General Discussion of Averages. Uniform Distribution of Directions of Velocities: In the preceding discussion it was seen that the pressure of a gas is determined by averaging over a large number of collisions. Similar considerations will frequently be used in the following pages. The next application will be to the directions of the velocities of the molecules, for the provisional assumption that the molecules could be divided into three equal groups, each moving parallel to a side of the box, was obviously only an approximation. Returning to the picture of a one-dimensional gas composed of molecules always moving parallel to a given edge of the box it is apparent that these molecules will not collide with each other. This state, however, is unstable since a small disturbance will cause a single molecule to move at an angle to the others and sooner or later collide with them, forcing them out of the original path. Thus, the original motion in a single direction will quickly change to one in which all directions appear in a uniform distribution. It may be assumed that in an ordinary gas, all directions of velocity appear equally often. For the justification of this assumption, it may be stated that, in the absence of external forces, there is no reason for the favoring of any special direction. It will be shown on p. 81 that the shape of the containing vessel does not invalidate the last statement. Until then the container will be assumed to be a sphere. The situation may be represented by the following construction. Consider an ordinary system of rectangular coordinates (Fig. 2) and a single molecule with components of velocity ξ, η, ζ, and, accordingly, components

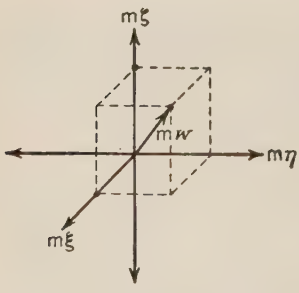

Fig. 2.

of momentum, $m\xi$, $m\eta$, $m\zeta$. The momentum of the molecule may be represented in this system of axes by the point $m\xi$, $m\eta$, $m\zeta$. Conversely, the position of the point uniquely determines the components of momentum and therefore the velocity. If the origin is connected to this "statepoint" the radius vector has the direction of the momentum (and velocity) of the molecule. This construction is to be carried out for all the molecules of the gas under consideration. The end points of these momentum vectors then give an exact picture of the directions of the momenta of all the molecules. Since the molecular velocities are supposed, for the present, to be of equal magnitude, all the endpoints will lie on a sphere of radius

$$m\sqrt{\xi^2 + \eta^2 + \zeta^2} = m|w|, \tag{13}$$

where $|w|$ is the magnitude of the common velocity.

If the velocities are distributed uniformly over all directions, the points will lie on the sphere with uniform density (an isotropic distribution). If the points are represented by black dots upon a white ground, the surface of the sphere will appear uniformly gray. The "number of molecules moving in a *definite* direction" has no meaning since a definite direction corresponds to a single point on the sphere and it cannot be expected that one of the black dots, representing the endpoint of a momentum vector, will *exactly* coincide with this single point. Rather must the question be worded so that a definite latitude is allowed for the variation of the direction, that is, the given direction must be surrounded with an element of solid angle $d\omega$.[1] In the present representation this means the evaluation of the number of endpoints lying in a small area circumscribed about the given point. This evaluation has a meaning only when the whole area can be regarded as uniformly gray. In other words, the elementary area must contain a large number of dots. If the area is too small the exact position of its boundary becomes of importance and small changes in shape without appreciable changes in size will cause a *relatively* large change in the color content (number of included end points) since another dot may be taken into or excluded from the area (Fig. 3).

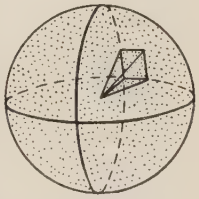

FIG. 3.

Such elementary areas and, in general, all magnitudes whose definitions require similar limitations are called "physically infinitely small."

If the density of the points on the surface of the sphere is designated by σ

$$N = \int \sigma d\omega, \tag{14}$$

since all the molecules must be represented somewhere on the sphere.

The fraction of the total number of molecules whose representative points lie within a given elementary area, $d\omega$, is

$$\frac{dN}{N} = \frac{\sigma d\omega}{\int \sigma d\omega}. \tag{15}$$

[1] It is not necessary that this elementary cone have a circular cross section.

In the case of the isotropic distribution the density, σ, is constant. Therefore

$$\frac{dN}{N} = \frac{d\omega}{\int d\omega} = \frac{d\omega}{4\pi} \tag{16}$$

is the fraction of the total number of molecules present whose velocities have directions included in the elementary solid angle $d\omega$ circumscribed about a given direction.

Instead of observing at a single instant all the molecules of a gas (space average) a single molecule may be followed for a long period of time. For example, the direction of its velocity may be recorded at a definite instant and at succeeding intervals of 1/1000 second. The different directions of motion of the same molecule so obtained may be plotted exactly as in the former case in which the velocities of different molecules were recorded simultaneously. In this case the sequence of the individual velocity vectors is of no importance, just as in the former case the relative position of the individual molecules did not come into consideration. Using this method there is obtained a picture identical with the former, containing more or less points corresponding to the number of observations taken. Thus, if there are too few molecules to give a sufficiently uniform coloring to the surface of the sphere, the usual space average may be replaced with a "time average" in which velocities to be compared are observed over a period of time rather than simultaneously.

FIG. 4.

FIG. 5

It is obvious that a single molecule reflected from the walls of a containing vessel travels equally often in any direction, as was originally stated (Fig. 4). Exception to this must be made in the case of certain special periodic motions (Fig. 5) which, however, revert to the usual behaviour upon the slightest disturbance.

After these general remarks, it will now be shown that the isotropic distribution of velocities is not affected by the shape of the containing vessel. To do this it will first be demonstrated that if such a distribution is present it will remain unchanged upon the introduction of a plane surface into the gas (Fig. 6).

Consider a molecule, a, approaching from the right along the path A. According to the law of reflection this molecule bounces off the plane along the path B. Now there is always another molecule, b,[1] which approaches the plane from the left along the path C, where C has the same direction as B.

[1] As a result of the isotropic distribution there are just as many molecules of type b as there are of type a. Naturally, the directions are not *exactly* fixed.

The molecule b bounces off along the path D which is A produced. In the absence of the surface the molecule a would traverse the path $A + D$ and the molecule b the path $C + B$. On account of the presence of the surface, a moves along $A + B$ and b along $C + D$. Thus, the only effect of the presence of the surface is to exchange the identities of the molecules in a definite path, i.e. moving in a definite direction. The molecule, a, accordingly, moves on B instead of the molecule b, and the sequence of events is changed. Neither of these circumstances is of importance. Therefore, the introduction of a plane surface does not disturb an existing uniform distribution of directions of motion. A non-uniform distribution, such as is present in a *flowing* gas, is obviously changed, since the deflected molecules are not compensated by those on the other side. A surface, accordingly, influences the flow of gases.

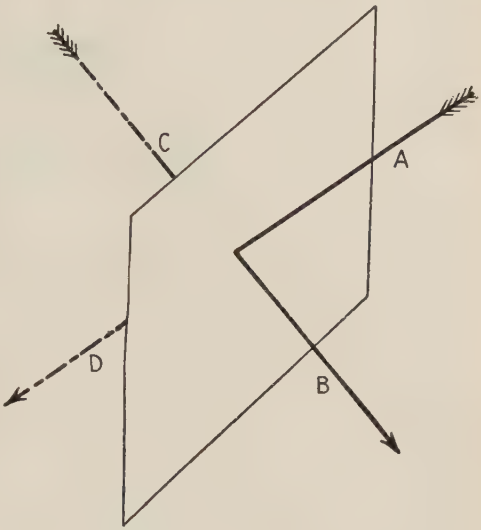

FIG. 6.

Furthermore, the conclusion is still valid if the plane is replaced by any irregular solid body, but in this case groups of more than two molecules must be considered. It must be noted that it has been unnecessary to refer to the collisions between molecules in the foregoing demonstration.[1]

It has just been shown that the insertion of a plane surface into a gas originally possessing a uniform distribution of directions of velocities, causes no change in this distribution. The same statement holds true for the wall of the containing vessel. If a uniform distribution obtains at any wall, the presence of the wall does not alter the distribution, but acts as if the mirror image of the actual gas were on the other side. In the case of gas flows, however, the effect of the wall cannot be neglected.

The Number of Collisions with the Wall. A More Exact Calculation of the Pressure: The calculation of the pressure of the gas may now be made more exact by a consideration of those molecules which approach the wall of

[1] This demonstration disproves the contentions of A. Fairbourne (*Phil. Mag.*, **43**, 1047 (1922); also H. H. Platt, *ibid.*, **45**, 415 (1923). Fairbourne attempted to show that differences of pressure would be set up by the introduction of a funnel-shaped solid into an attenuated gas. He neglected, however, the compensating effect of collisions on the outside of the funnel. See also R. d'E. Atkinson, *Nature*, **111**, 326 (1923); E. Witmer, *Phil. Mag.*, **47**, 152 (1924); and J. Fisher, *ibid.*, **47**, 779 (1924).

the container at an angle. Consider a system of space polar coordinates, the origin placed on the wall and the polar axis perpendicular to it (Fig. 7).

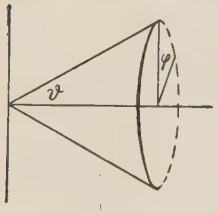

Fig. 7.

The number of molecules colliding with 1 sq. cm. of the wall in unit time and coming from the direction ϑ, φ will now be calculated. Here, of course, by the direction ϑ, φ is meant the cone of solid angle $d\omega = \sin \vartheta d\vartheta d\varphi$ circumscribed about the direction ϑ, φ. Obviously, only those molecules which possess velocities in this direction can come from this direction. The number of molecules in 1 cc. will be designated by N/v, where N is the total number of molecules and v is the total volume. Of these $\frac{N}{v}\frac{d\omega}{4\pi}$ have the given direction. Those molecules whose velocities possess the prescribed direction and which are contained in an inclined cylinder, erected on an area of 1 sq. cm., of length w, and axis along the given direction (Fig. 8) will collide with the wall in one second. This is apparent since the last molecule, which was originally at the end of the cylinder, has, after one second has elapsed, traversed a length of w cm. and hence has just collided. Those in front of it clearly reached the wall earlier. Since collisions between molecules merely exchange individuals and do not affect the number of molecules in this group, such collisions need not be taken into account. The volume of the cylinder is $w.1$ cm^2. cos ϑ, therefore the number of molecules coming from the given direction is

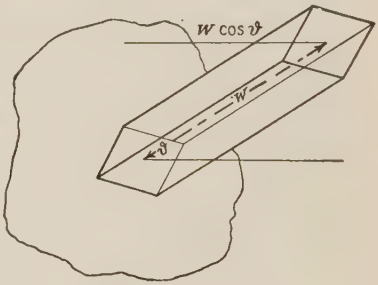

Fig. 8.

$$\frac{N}{v}.w.\ \cos\vartheta\frac{d\omega}{4\pi} = \frac{N}{4\pi v} w \cos\vartheta \sin\vartheta d\vartheta d\varphi. \tag{17}$$

The total number of collisions per unit area of the wall in unit time is found by integration over the hemisphere, giving φ the limits 0 to 2π and ϑ the limits 0 to $\pi/2$, the result being

$$\frac{w}{4}\frac{N}{v}. \tag{17'}$$

In the calculation of the pressure it is to be observed that on collision with the wall only the normal component, w cos ϑ, of the velocity is reversed, the tangential component remaining unchanged. The change of momentum per collision is therefore

$$2mw \cos\vartheta.$$

For all the collisions by molecules coming from the direction ϑ, φ, per second, it is

$$\frac{N}{v} 2mw \cos \vartheta . \frac{w}{4\pi} \cos \vartheta \sin \vartheta d\vartheta d\varphi, \tag{18}$$

which after integrating becomes

$$\frac{N}{v} \frac{mw^2}{3} \tag{19}$$

as in the approximate calculation (equations (9) and (10)). This accidental agreement is caused by the appearance of $\cos^2 \vartheta$ in the expression for the pressure, the average value of this term over the hemisphere being

$$\overline{\cos^2 \vartheta} = \frac{\int_0^{\pi/2} \cos^2 \vartheta \sin \vartheta d\vartheta \int_0^{2\pi} d\varphi}{2\pi} = \frac{1}{3}. \tag{20}$$

The exact calculation of the number of collisions contains

$$\frac{1}{2} \overline{\cos \vartheta} = \frac{1}{4}, \tag{20'}$$

whereas the approximate calculation would have given 1/6.

Equalization of Velocities; Temperature: Collisions between the molecules have been disregarded until now, except when used to give a uniform distribution of *directions* of motion. They are also influential in determining the magnitudes of the velocities. Even if, as has been previously assumed, all the molecules of a gas had exactly the same speed, collisions would soon change this state, exactly as on p. 78 the one-dimensional motion was transformed into some other distribution. For the sake of simplicity the molecules will be assumed to be perfectly elastic spheres in the following discussion. The laws governing the collisions between such spheres are readily stated as follows: If the centers of two colliding spheres are connected at the moment of collision by the "line of centers," the components of the two velocities perpendicular to this direction remain unchanged, while the components along the line of centers after collision are connected with the components before collision by the relations:

$$w_{1z} = \frac{m_1 - m_2}{m_1 + m_2} w_{1z}^0 + 2 \frac{m_2}{m_1 + m_2} w_{2z}^0, \tag{21}$$

$$w_{2z} = \frac{m_2 - m_1}{m_1 + m_2} w_{2z}^0 + 2 \frac{m_1}{m_1 + m_2} w_{1z}^0. \tag{22}$$

If the two masses are equal, the velocity components along the line of centers are merely interchanged. In this case it is easily shown how two originally equal speeds may be changed upon collision. Suppose two molecules

collide in the manner shown in Fig. 9. The entire initial speed of the first is parallel to the line of centers. The second has an equal speed perpendicular to that of the first, thus having no component of velocity parallel to the line of centers. After the collision the first sphere has no velocity parallel to the line of centers. The component perpendicular to this remains unchanged; since this latter component was originally zero, the sphere is brought to a complete stop. The velocity of the second is the sum of two equal and perpendicular components. The molecule is therefore deflected from its original path through 45° and moves off with a speed $\sqrt{2}$ times as great as its original speed.

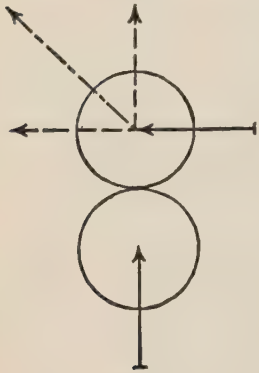

FIG. 8.

The collisions accordingly change the velocities of the molecules not only in direction but also in magnitude. This fact will be developed below from the condition that the distribution is produced by collisions and, once set up, remains undisturbed. In any case, however, the kinetic energy of the whole gas is equal to the sum of the kinetic energies of the constituent molecules. In the pressure equation there must now be inserted

$$\frac{N}{N_A} U_k = \frac{\sum mw^2}{2} \tag{23}$$

instead of

$$\frac{N}{N_A} U_k = \frac{Nmw^2}{2}, \tag{10}$$

where the summation is to be extended over all the molecules. Moreover, the " mean square velocity " may be defined by

$$\overline{w^2} = \frac{\sum w^2}{N}, \tag{24}$$

$$\frac{N}{N_A} U_k = \frac{Nm\overline{w^2}}{2}. \tag{25}$$

The relation between the kinetic energy, U_k, and the temperature will now be considered. The fundamental fact necessary for the definition of temperature is that, according to experience, when two bodies are placed in " thermal contact " the exchange of energy ceases after a sufficiently long time. When in this state the two bodies are, by definition, said to have the same temperature. On the other hand, the scale by which numbers may be given to different temperatures is a matter of pure convention.

Accordingly, the relation between the mean energies ($m_1\overline{w_1}^2/2$ and $m_2\overline{w_2}^2/2$) of the molecules of two gases in thermal equilibrium must now be found. (The total number of molecules is unimportant since a decrease in the number of

molecules present, together with a corresponding decrease in volume, in no way affects the collisions or, therefore, the energy transfer). It is possible to proceed in two ways: In the first place it may be stated that it is known from experiment that if two gases have the same pressure-volume product and if their two masses are proportional to their respective molecular weights, (in which case they contain the same number of molecules since $N.m$ equals the total weight), then the two gases are in thermal equilibrium and are therefore, by definition, at the same temperature.[1]

But since it has been shown that

$$\frac{3pv}{2N} = \frac{m\overline{w^2}}{2} \tag{25'}$$

it follows from the equality of pv/N for all gases at the same temperature that $m\overline{w^2}/2$ is the same for all gases at a given temperature, regardless of the individual values of pressure and volume (or density), and the nature of the gas.

From this it follows that for all gases $m\overline{w^2}/2$ is a function of the temperature alone and, moreover, is the same function for all gases. That this quantity should be made proportional to the temperature, or, more precisely, that

$$\frac{m\overline{w^2}}{2} = \frac{3}{2}\frac{RT}{N_A}, \tag{26}$$

where R is the gas constant and N_A the number of molecules contained in one mol, is a purely arbitrary choice by which the volume of the gas in a constant pressure gas thermometer is taken to be directly proportional to the absolute temperature.

This demonstration gives no kinetic explanation of the fact that no heat is exchanged between two gases if their molecules have, on the average, equal amounts of energy. It has only been stated that the theory must lead to this conclusion in order that it shall agree with experience.

The second method of arriving at a kinetic definition of temperature is to *deduce* kinetically the foregoing law and therewith prove the empirical relation

$$pV = RT, \tag{27}$$

where V is the volume of one mol.

Consider first two different gases which have the same molecular weight and which are confined in the same container. In the course of time their average energies will become equal. To show this, suppose that the molecules

[1] The following procedure is more exact: Two equal quantities of the same gas exchange no heat if they have the same pressure-volume product. A second gas may now be brought to such a condition that, if placed in thermal contact with the first, there will be no heat transfer. By suitable adjustment of the mass of this second gas it may be made to have the same pressure-volume product as the first. It is then found that the masses of the two gases are in the ratio of small multiples of the two combining weights. If this ratio of the masses has been determined for any given value of the pressure-volume product, it remains constant for all values of the pressure-volume product. (Avogadro's Law.)

of the first gas originally possessed an average energy greater than that associated with the molecules of the second. It is apparent that if in any gas a molecule acquires an especially high velocity, it will soon distribute this velocity among the other molecules. The result of a collision, however, depends only on the masses of the colliding spheres and not on their size and other properties. Therefore the high velocities of the molecules of the first gas will be distributed among the molecules of the second and at equilibrium the two types of molecules will have the same average energy per molecule because the only property of the molecule which enters into the equations of collision is its mass.

It will now be supposed[1] that the gases are at different densities and separated by a medium which will permit conduction of heat in such a way that the mechanism of this conduction can be completely understood. For this purpose the "thermal" contact between the two gases A and B (Fig. 10) will be made through a thin layer of gas separated from the gas A by the wall a. This wall is supposed to offer no resistance to the free passage of the molecules of gas A, but is to be completely impermeable to molecules of gas B.[2] Similarly the dividing wall between the thin layer and the main body of gas B is to be permeable to gas B and is impermeable to gas A. The containing vessel for gas A reaches to the wall b (since a offers no resistance to the molecules A) and in the intermediate layer A has the same density as in its container proper. Similar statements hold for gas B with respect to wall a. If it is now assumed that the molecules A have originally a higher mean velocity than those of gas B, some of the molecules of A in the intermediate space will collide with molecules of B and in this manner lose energy according to the previous discussion, because the intermediate space is simply a mixture of A and B, and it is naturally immaterial to the individual collisions whether or not containers of the pure gases are attached to the outside of the container of the mixture.

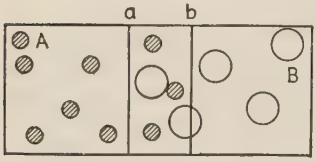

Fig. 10.

As the result of the collisions in the intermediate layer the molecules of A are returned to the main body of A with less energy, on the average, than that with which they left. Those molecules which have remained in the A compartment give up energy to the returning molecules by means of collisions, that is, the returning molecules take up energy and reenter the intermediate space with an amount of energy greater than that with which they left but which is less than their original energy. On the other hand the molecules of gas B return from the intermediate layer with an increased energy which they proceed to give up to the other molecules in the B compartment. It is seen that the intermediate layer exchanges heat from one gas to the other

[1] L. Boltzmann and G. Bryan, *Wien. Ber.*, **103**, 1125 (1894); *Proc. Phys. Soc.*, **13**, 485 (1895).

[2] Whether or not it is possible to make such a wall is beside the point. It is only necessary that the discussion does not contradict itself.

without disturbing the given differences in density. This heat transfer takes place from the gas of high kinetic energy to the gas of low kinetic energy. The two gases are in thermal equilibrium only if the molecules of one gas transfer no energy in the intermediate space to the molecules of the other. The exchange of heat in the intermediate layer stops, however, only when the molecules of gas A and gas B each have the same average kinetic energy.

It has thus been proven kinetically that two gases of the same molecular weight are in thermal equilibrium (and are therefore at the same temperature) if the average kinetic energies of their molecules are equal.

This proof must now be extended in two directions.

It must first be shown that the result is independent of the nature of the heat conducting wall. This, however, would require a general knowledge of such walls. Since the theory of gases gives no information on the subject, this generalization can only be made by means of the methods of general statistical mechanics.

Secondly it must be shown that in a mixture of gases of different molecular weight each constituent has, on the average, the same mean kinetic energy per molecule. If this be proven, it can be demonstrated exactly as before that when two gases are in thermal contact they do exchange heat only if their molecules have different mean kinetic energies. In other words, it is proven that for all gases, regardless of nature and density, the temperature is determined by the kinetic energy alone. It is then natural to set the temperature proportional to the energy. However the proof of the equalization of energy in a mixture of gases of different molecular weights can only be carried out after Maxwell's Law of the Distribution of velocities has also been proven.[1] Until that time the general validity of the equation

$$\frac{2}{3}\frac{N_A m\overline{w^2}}{2} = RT \tag{28}$$

must be assumed from experience. From it the equalization of energy in mixtures of gases follows without restrictions.

Dalton's law of Partial Pressures follows at once from this result. It has already been shown on p. 77 that, in a mixture of gases,

$$p = \frac{N_1}{v}\frac{m_1\overline{w_1^2}}{3} + \frac{N_2}{v}\frac{m_2\overline{w_2^2}}{3} + \cdots. \tag{11}$$

That is, the total pressure is built up of the partial pressures

$$\left.\begin{aligned} p_1 &= \frac{N_1}{v}\frac{m_1\overline{w_1^2}}{3}, \\ p_2 &= \frac{N_2}{v}\frac{m_2\overline{w_2^2}}{3} \end{aligned}\right\} \tag{29}$$

[1] The proof indicated by Gans-Weber, *Repertorium der Physik*, I_2, 366 Leipzig (1916) requires the distribution law. L. Boltzmann, *Wien. Ber.*, **94**, 613 (1886).

Each of these partial pressures is, however, the pressure which would be exerted by the corresponding gas if it were present alone with a temperature and volume equal to the given temperature and volume because, as has just been demonstrated, this quantity $m_i\overline{w_i^2}/2$ depends only on the temperature and not upon the density or presence of another gas.

The Kinetic Energy and Specific Heat of a Monatomic Gas: The total energy content of those molecules which may be regarded as points is the kinetic energy just discussed, which is

$$U_k = \frac{3}{2}RT. \tag{30}$$

The molar heat at constant volume is therefore

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = \frac{3}{2}R. \tag{31}$$

The energy content and specific heat at constant volume are independent of the volume because the only energy associated with the gas is the mean kinetic energy of the molecules, which depends only on the temperature. Since it is known experimentally that many gases have higher specific heats than that calculated above, it is concluded that such gases contain other types of energy. It will be shown later that these are contributed by the rotation of the molecules and motions within the molecules.

The kinetic energy of the translatory motion can be resolved along the three axes of an arbitrarily oriented system of coordinates. If this is done

$$w^2 = \xi^2 + \eta^2 + \zeta^2, \tag{32}$$

where ξ, η, ζ are the components of w along the X, Y, and Z axes respectively. Then

$$U_k = N_A\frac{m}{2}\overline{w^2} = \frac{m}{2}\sum w^2 = \frac{m}{2}\sum(\xi^2 + \eta^2 + \zeta^2) = \frac{N_A m}{2}(\overline{\xi^2} + \overline{\eta^2} + \overline{\zeta^2}). \tag{33}$$

Since, on the average, no particular direction can be especially favored,

$$\overline{\xi^2} = \overline{\eta^2} = \overline{\zeta^2} = \frac{\overline{w^2}}{3}. \tag{34}$$

A more rigorous proof of this statement may be obtained by using the methods of p. 83. Since $\xi = w\cos\vartheta$, $\overline{\xi^2} = \overline{w^2}\,\overline{\cos^2\vartheta}$. The averaging over the directions has been carried out previously and since

$$\overline{\cos^2\vartheta} = \frac{1}{3}, \tag{20}$$

$$\overline{\xi^2} = \frac{\overline{w^2}}{3} \tag{35}$$

The magnitude of w is still to be averaged, as indicated by the bar over the symbol w.[1] The particular orientation of the axes is unimportant since, on the average, the directions of the molecular velocities are distributed uniformly.

The mean kinetic energy associated with each axis is

$$\frac{3}{2}\frac{RT}{3} = \frac{RT}{2}. \tag{33'}$$

Thus a " one dimensional gas " would have a specific heat $R/2$. For a two dimensional gas, whose molecules are constrained to move in a plane,

$$C_v = 2R/2.$$

The mean square velocity of the molecules can now be calculated, since

$$U_k = N_A m\frac{\overline{w^2}}{2} = M\frac{\overline{w^2}}{2} = \frac{3}{2}RT. \tag{36}$$

With $R = 8.315 \times 10^7$ ergs per degree per mol., there is obtained

$$\overline{w^2} = 2.4945 \times 10^8 \frac{T}{M} \text{ cm}^2/\text{sec.}^2 \tag{37}$$

For hydrogen at 0° C.,

$$\sqrt{\overline{w^2}} = 1838 \text{ m./sec.}$$

For other gases and temperatures this quantity may be calculated from the fact that it is directly proportional to the square root of T and inversely proportional to the square root of the molecular weight.

The Work Done by the Expansion of a Gas: The thermodynamically important process of the expansion of a gas will now be treated from the kinetic viewpoint. The two fundamental cases of adiabatic expansion to be considered are the irreversible process in which the work done equals zero and the reversible process in which a definite amount of work is performed.

For the discussion of the first case, which is realized in the Gay-Lussac experiment, consider a thermally insulated vessel divided into two parts. One half of the vessel is filled with a moderately dilute gas, the other half evacuated. Internal equilibrium is assumed to have been established in the gas. The dividing wall is now quickly removed in its own plane, in the manner of a sliding door. The molecules moving toward the empty half are in no way affected by this removal. The only change produced in the system is that they can now move further and are not reflected back again until they encounter a wall of the formerly empty half. Their kinetic energy remains unchanged but, especially in the previously evacuated portion, there is now a favored direction of velocity.[2] This, however, is soon obliterated by the

[1] That w is not the same for all molecules at a given instant will be shown on p. 94. Cf. also p. 84.

[2] The excess of molecules with a velocity along the favored direction must take place at the expense of the number of molecules with velocities along the other directions. *During* the motion, therefore, the kinetic energy of the chaotic motion, and hence the temperature, is decreased, as a result of the mass motion of the gas.

collisions between the molecules. The increase in volume has in no way affected the magnitude of the molecular velocities, and therefore the kinetic energy of the gas is unchanged. Since the temperature of the gas is determined by the kinetic energy alone, the experiment causes no permanent temperature change. On the other hand, this conclusion could be assumed and the fact that the kinetic energy of a gas depends only on the temperature, that is, is independent of the density, could be derived from the experimental result.

If work is done during the expansion of the gas the situation is quite different. Consider, as on p. 76, a single molecule moving exactly perpendicular to the piston shown in Fig. 1. The piston is moved out with the velocity w'. In the treatment of collisions with the piston it is necessary to use the velocity of the molecule relative to the piston.[1] The molecule which has an absolute velocity w (absolute, that is, with respect to the containing vessel) has a velocity relative to the piston equal to $w - w'$. Upon collision with the piston it is not brought to absolute rest, but only to rest with respect to the piston, i.e. it continues to move for a short time in contact with the piston. The momentum given to the piston is therefore

$$m(w - w'). \tag{38}$$

The same amount of momentum is again given to the piston upon the recoil of the molecule. The total momentum gained by the piston is therefore

$$2m(w - w'). \tag{39}$$

The molecule rebounds with a velocity relative to the piston equal to $w - w'$. Its absolute velocity has been decreased to $w - 2w'$.[2] The kinetic energy of the molecule has been decreased by an amount equal to[3]

$$\frac{mw^2}{2} - \frac{m(w - 2w')^2}{2} = 2mw'(w - w'). \tag{40}$$

If $\mathbf{N}dt$ is the number of collisions with the piston in the time dt, the energy decrease of the gas in the same time is

$$-du = 2mw'(w - w')\mathbf{N}dt. \tag{41}$$

On the other hand it has been shown that the force on the piston is

$$2m(w - w')\mathbf{N}. \tag{41'}$$

The work done by the molecule upon the piston is this force times the displace-

[1] In other words, a one dimensional gas is assumed, the piston being drawn out in the direction of motion of the gas molecules.

[2] This may also be shown as follows: The initial momentum of the molecule in the direction of motion of the piston is mw. The momentum given to the piston equals $2m\ (w - w')$. The momentum remaining with the molecule is the difference of $mw - 2m(w - w') = -m(w - 2w')$. The molecule accordingly moves in the opposite direction with a velocity $w - 2w'$.

[3] R. Clausius, *Pogg. Ann.*, **100**, 366 (1857); Mechanische Wärmetheorie III, 2. ed., p. 29, Braunschweig (1891); A. Krönig, *Pogg. Ann.*, **99**, 322 (1856) (the latter paper is qualitative).

ment of the piston $w'dt$ and is thus shown to be equal to the decrease in energy of the gas (41) as is demanded by the Law of Conservation of Energy.

The rate of the energy decrease may also be ascertained. It is necessary for this that the process be carried out reversibly or quasistatically that is, w' is negligibly small compared to w. The decrease in the energy of a molecule upon collision is then

$$2mw'w. \tag{42}$$

The number of collisions with the piston may be calculated with sufficient accuracy by putting it equal to the number of collisions with a stationary piston. This quantity is

$$\frac{w}{2l_1}dt. \tag{43}$$

The total decrease in energy in the time dt is therefore

$$-d\left(\frac{mw^2}{2}\right) = 2mw'w\frac{w}{2l_1}dt. \tag{44}$$

In the same time the piston has been displaced an amount $dl_1 = w'dt$. Thus

$$-\frac{d\frac{mw^2}{2}}{dl_1} = \frac{m\frac{w'w^2}{l_1}dt}{w'dt} = \frac{mw^2}{l_1} \tag{45}$$

or

$$-\frac{d\frac{mw^2}{2}}{mw^2} = \frac{dl_1}{l_1}. \tag{46}$$

Upon integrating

$$-ln(mw^2) = 2lnl_1 + \text{constant} \tag{47}$$

or, since mw^2 is in this case equal to

$$pl_1l_2l_3; \qquad \text{and} \qquad l_1 = \frac{v}{l_2l_3}$$

upon changing the form of the integration constant, the equation for the reversible adiabatic expansion of a gas is found to be

$$pv^3 = p_0v_0^3. \tag{48}$$

If, instead of a single molecule, there are any number N, which do not collide with each other, Nm appears in the place of m throughout the demonstration and the final relation remains unchanged.

Equation (48) is interesting in several respects. In the first place it shows how a finite amount of work may be done even though the piston is moved infinitely slowly as required by the condition of reversibility. For although by (40) the work done in a single collision is directly proportional to the piston

velocity, w', and is therefore infinitely small, the number of collisions for a given displacement is inversely proportional to w' and, for an infinitely slow motion, becomes infinitely large. Thus, in equation (45), which gives the work done for a given piston displacement (volume change), w' appears in both numerator and denominator and hence cancels out. The equation of the reversible adiabatic change developed in thermodynamics is

$$pv^{Cp/Cv} = p_0 v_0^{Cp/Cv}. \tag{49}$$

In the present case, therefore, C_p/C_v must equal 3. This is in fact the case, since the considerations have dealt with a one dimensional gas for which

$$C_v = \frac{1}{2}R \qquad \text{and} \qquad C_p = C_v + R = \frac{3}{2}R.^1$$

Equation (48) is therefore in complete agreement with thermodynamics.

In the case of a three dimensional gas only the component of velocity normal to the piston is diminished; the components in the plane of the piston remaining unchanged during a collision.

The decrease in energy per collision then becomes

$$2mww' \cos \vartheta. \tag{50}$$

The collisions between the molecules, if the piston velocity is sufficiently low, preserve the uniform distribution of the velocities which would otherwise be disturbed by the motion of the piston.

The decrease in energy during the displacement dl_1, is

$$-\frac{d\dfrac{Nmw^2}{2}}{dl_1} = \frac{Nmw^2}{l_1}\overline{\cos^2 \vartheta} = \frac{Nmw^2}{3l_1}. \tag{51}$$

From this

$$-ln(Nmw^2) = \frac{2}{3}lnl_1 + \text{constant}; \tag{52}$$

accordingly

$$pv^{5/3} = p_0 v_0^{5/3} \tag{53}$$

as must now be the case.

It is further seen from the demonstration that if the piston velocity is too great to be neglected in comparison with w, the pressure and therefore also the work done is less than in the quasistatic case.[2] Moreover, upon compression,

[1] See Chapter II.

[2] In this general case the formulas become so complicated that they do not allow an explicit evaluation. Returning to the one dimensional case and designating initial values with the subscript zero, values at the end of the s'th collision with the subscript s and the time between the s'th and the $(s+1)$'th collision with τ_s, then the following relations may be written:

$$w_s = w_0 - 2sw'$$

$$\tau_s = \frac{l_s + l_{s+1}}{w_s}.$$

(w' negative), the pressure and the work done on the gas are greater than in the infinitely slow process. This is also in agreement with thermodynamics.

The Barometric Formula and Maxwell's Law of Distribution of Velocities: [1] Consider a column of gas at equilibrium in a constant gravitational field. It is known from thermodynamics that the whole column must be at the same temperature. Consider now a thin horizontal layer of thickness dx and cross-section equal to 1 sq. cm. The weight of this layer is

$$cgMdx, \tag{54}$$

where g is the acceleration of gravity, c the number of mols in one cubic centimeter, that is $\frac{N}{v} \cdot \frac{1}{N_A}$ and M is the molecular weight. The pressure on the under side of the layer in question is greater than that on the upper side by the amount (54), or

$$-\frac{dp}{dx}dx = cgMdx \tag{55}$$

(x being measured vertically upward). Equation (55) is the familiar hydrostatic formula.

Further

$$p = \frac{RT}{V} = cRT, \tag{56}$$

The displacement of the piston between two collisions is

$$l_{s+1} - l_s = w'\tau_s = \frac{l_s + l_{s+1}}{w_s}w',$$

From which there is obtained

$$l_{s+1} = l_s\frac{w_s + w'}{w_s - w'} = l_s\left[1 + \frac{2w'}{w_0 - (2s+1)w'}\right]$$

$$l_s = l_0\prod_1^s\left[1 + \frac{2w'}{w_0 - (2s-1)w'}\right].$$

The symbol $\prod_1^s$ means that the s in the bracket is to be given in turn all integral values from 1 to s. The s terms so formed are all to be multiplied together. Thus Π (multiple product) is analogous to the summation symbol Σ.

This equation determines the number s of collisions which have occurred up to a definite position of the piston, l_s. On taking the logarithm of this last expression and replacing the summation with an integration, there is obtained

$$ln\frac{l}{l_0} = ln\frac{V}{V_0} = \left(\frac{w_0}{2w'} + \frac{3}{2}\right)ln\frac{w_0 + 3w'}{w + 3w'} - \left(\frac{w_0}{2w'} + \frac{1}{2}\right)ln\frac{w_0 + w'}{w + w'} + \frac{w_0 - w}{2w'}ln\frac{w + 3w'}{w + w'},$$

which gives for small values of w'/w_0

$$2ln\frac{V}{V_0} = -ln\frac{mw^2}{mw_0^2} + 4w'\left(\frac{1}{w_0} - \frac{1}{w}\right).$$

The decrease in energy is

$$\sum_1^s 2mw'(w_{s-1} - w') = \Sigma 2mw'[w_0 - (2s-1)w'] = 2mw'(sw_0 - s^2w').$$

[1] L. Boltzmann, *Wien. Ber.*, **74**, 503 (1876); G. Jäger, *ibid.*, **112**, 309 (1903).

where V is the molar volume. Accordingly

$$-\frac{d(cT)}{dx} = \frac{Mg}{R}c. \tag{57}$$

Since the system is in thermal equilibrium, T is constant, and

$$ln\, c = -\frac{Mg}{RT}x + ln\, c_0, \qquad c = c_0 e^{-\frac{Mgx}{RT}} \tag{58}$$

or

$$p = p_0 e^{-\frac{Mgx}{RT}}, \tag{59}$$

where c_0 and p_0 signify respectively the concentration and pressure at sea-level ($x = 0$). This formula gives the decrease in atmospheric pressure with altitude. Actually, however, temperature differences are present in the air which cause deviations from the equilibrium state.

The discussion from the kinetic standpoint is as follows. Imagine the gas again to be one-dimensional in the X-direction, neglecting, therefore, the momenta along the Y- and Z-axes. The effect of collisions will also be neglected for the present. If all the molecules had the same velocity, the behavior of the gas would be quite different from that required by thermodynamics. The molecules starting up from sea level with a velocity w_0 would lose their kinetic energy according to the equation

$$\frac{mw^2}{2} = \frac{mw_0^2}{2} - mgx. \tag{60}$$

At the height $x = w_0^2/2g$ they would all stop and fall back to the earth, finally regaining their original kinetic energy. The atmosphere would accordingly have a sharp upper limit and its temperature would decrease linearly with the altitude until it reached the absolute zero. The density, however, would increase with the altitude since, in the upper regions, the molecules would move more slowly and therefore require a longer time to traverse a given interval. These conclusions are changed slightly on taking into account the horizontal components of the velocity, but the sharp limit and the decrease of the temperature remain unchanged. To obtain agreement with the thermodynamic treatment it is therefore necessary to conclude that the molecules cannot all have the same velocity, as has already been shown from the law of collisions.

That distribution of velocities which will permit the temperature to remain constant throughout the column and at the same time satisfy equation (58) will now be determined.[1]

Just as it was formerly necessary to speak of the number of molecules having directions of velocity within a definite solid angle, it will now be necessary to consider the number of molecules having velocities whose magnitudes

[1] L. Boltzmann, *Wien. Ber.*, **74**, 503 (1876).

fall within certain limits. All the previous limitations placed upon the size of this limiting interval of velocities apply to the present case. The number of molecules having velocities between w and $w + dw$ (where dw is only physically, not mathematically infinitely small, cf. p. 79) will be designated by

$$dN = Nf(w)dw, \tag{61}$$

where N is the number of molecules in one cubic centimeter and $f(w)$ the fraction of the molecules fulfilling the specified requirements. In this section the subscript zero attached to a symbol will indicate that the quantity is measured at the bottom of the column, the subscript x referring to a height x above the bottom. It has already been shown that if N' molecules per cc. are moving parallel to each other with the velocity w, then, in the time dt, there will pass through unit area of a plane perpendicular to the direction of motion, the number

$$N'wdt. \tag{62}$$

In other words, the molecules passing the plane in a given time are the contents of a cylinder of unit cross-section and height wdt, since the last molecule in this cylinder will just pass the plane at the end of the time dt.

Consider now two planes at the heights x and $x + dx$. In the upper plane the density of the molecules must, according to (58), be smaller than that in the lower plane by the amount

$$N\frac{mg}{kT}dx = N_0 e^{-\frac{mgx}{kT}}\frac{mg}{kT}dx.^1 \tag{63}$$

This is only possible if certain molecules can pass the lower plane but cannot reach the upper one, stopping and falling back in the intermediate space. The number of molecules thus reversed per second per unit cross-section of the layer is

$$N_x\bar{w} - N_{x+dx}\bar{w} = N_0 e^{-\frac{mgx}{kT}}\bar{w}\frac{mg}{kT}dx. \tag{64}$$

Since the gas is at constant temperature, the mean velocity, $\bar{w}$, of the molecules is the same at all heights.

The velocities with which these molecules which are turned back bounce up from the bottom of the column must lie within such limits that the slowest can just pass the lower plane, that is

$$\frac{mw_0^2}{2} = mgx, \tag{65}$$

while the fastest must just reach the upper plane or

$$\frac{m(w_0 + dw_0)^2}{2} = mg(x + dx), \tag{66}$$

[1] $k = R/N_A = mR/M$; k is known as the Boltzmann constant.

whence

$$w_0 dw_0 = g dx \qquad \text{and} \qquad w_0 = \sqrt{2gx}. \tag{67}$$

The number of molecules per cc. having this velocity at the bottom is

$$N_0 f_0(w_0) dw_0. \tag{68}$$

The number leaving the bottom per second per unit cross section is

$$N_0 f(w_0) w_0 dw_0 = N_0 f_0(\sqrt{2gx}) g dx \tag{69}$$

after substitution of the values obtained in (65) and (67).

All these and only these molecules have as an upper limit to their paths the layer between x and $x + dx$. Upon reaching this layer, they fall back again. Equating (64) and (69) there is obtained

$$N_0 \bar{w} \frac{mg}{kT} e^{-\frac{mgx}{kT}} dx = N_0 f_0(\sqrt{2gx}) g dx \tag{70}$$

or

$$f_0(\sqrt{2gx}) = \frac{m\bar{w}}{kT} e^{-\frac{mgx}{kT}} = \frac{m\bar{w}}{kT} e^{-\frac{m}{2kT}(\sqrt{2gx})^2} \tag{71}$$

or

$$f_0(w_0) = \frac{m\bar{w}}{kT} e^{-\frac{mw_0^2}{2kT}} = A e^{-\frac{mw_0^2}{2kT}}. \tag{72}$$

This is the simplest form of the famous Maxwell Distribution law [1] which plays an outstanding part in the whole of the kinetic theory. The preceding discussion has only proved, however, that this relation must hold in order that the thermodynamic requirement of constancy of temperature be satisfied for a column of gas in equilibrium in a gravitational field, but no proof of this distribution law has been given on kinetic grounds. This proof when given, will be a kinetic explanation of the thermodynamical statement.

This distribution of velocities is clearly not the result of the gravitational field, since the strength of the field, g, does not appear in the formula. The effect of gravity is merely to separate the molecules into a " velocity spectrum."

Since the temperature is constant, the same distribution of velocities prevails throughout the entire column, that is, the relation

$$dN = NAe^{-\frac{mw^2}{2kT}} dw \tag{73}$$

represents the relative distribution of the velocities among the molecules. The quantity dN/N everywhere remains the same for a given value of w, only the *absolute* number of molecules varying with the height. Since, however, it may seem paradoxical that the *mean* kinetic energy is the same for different altitudes, the cause of this fact will be further explained.

Consider a definite group of molecules with velocities at the bottom of the

[1] Clerk Maxwell, *Phil. Mag.*, **19**, 22 (1860).

column between w_0 and $w_0 + dw_0$. As stated before, these velocities decrease after the molecules have risen to the height x to the value w given by the relation

$$w^2 = w_0^2 - 2gx. \tag{74}$$

Upon differentiating this, x being held constant, there is obtained the equation

$$wdw = w_0 dw_0, \tag{75}$$

that is, that the interval of the velocity limiting the number of molecules in this group is inversely proportional to the velocity itself. Physically, this equation means that, if any of the molecules of the group arrive at the layer under consideration, all of the molecules of the group will so arrive, that is, all the molecules bouncing up from the bottom with velocities between w_0 and $w_0 + dw_0$.

For a given number of molecules passing a plane, the density is seen to be inversely proportional to the velocity upon inversion of the statement on page 95. The number of molecules in the group under consideration is

$$N_0 A e^{-\frac{mw_0^2}{2kT}} w_0 dw_0. \tag{76}$$

All these pass in one second through 1 sq. cm. at the height x and at this height have a velocity w, if $2gx < w_0^2$. The density at x is therefore

$$N_0 A e^{-\frac{mw_0^2}{2kT}} \frac{w_0 dw_0}{w}. \tag{77}$$

On introducing (74) and (75) there is obtained

$$N_0 A e^{-\frac{\left(\frac{mw^2}{2} + mgx\right)}{kT}} dw = N_0 A e^{-\frac{mgx}{kT}} e^{-\frac{mw^2}{2kT}} dw = NA e^{-\frac{mw^2}{2kT}} dw, \tag{78}$$

which is merely the Maxwell Law for the density N and velocity w at the height x.

It will now be apparent why the mean kinetic energy is independent of the altitude. Roughly speaking the total kinetic energy of a group of molecules is decreased as the group moves upward, but at the same time the number of molecules is decreasing due to the dropping out of the slower ones. This dropping out takes place in such a manner that the average kinetic energy per molecule remains constant.[1] This constancy is made possible by the particular

[1] Perhaps this may be further clarified by the following example: Coins (energy) are distributed among a number of people (molecules) according to an exponential law. Then

Number of coins (E) per person	0	1	2	3	4	5	6
" " persons possessing E coins	64	32	16	8	4	2	1

The equation expressing this distribution is

$$64 \times 2^{-E} = 64e^{-E\ln 2}.$$

form of Maxwell's Law, from which it follows that if dN is plotted [1] as a function of w^2 and part of the curve cut off by erecting a new ordinate axis at w_1^2, the curve to the right of the new axis is equivalent to that which would be obtained if the energy of each molecule were decreased by a constant amount. It is now seen that the right hand portion of the curve again represents a Maxwellian distribution of the remaining molecules (Fig. 11). Geometrically this means that the curve lying to the right of the new axis is a replica, on a smaller scale, of the original curve.

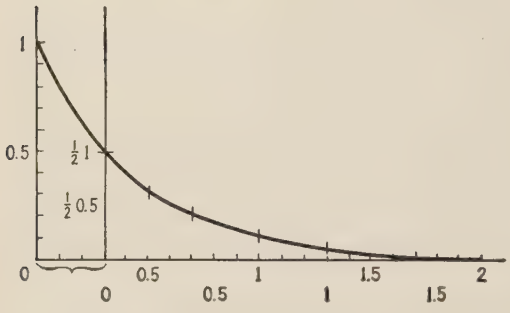

FIG. 11.

Throughout this discussion it has been assumed that the molecules move only in a vertical direction and that they do not collide with each other. These limitations will now be removed successively. If, in the first place, the molecules moving up are allowed to collide with those coming down, the sole effect is to exchange the velocities of the colliding molecules. For example: If there are no collisions, molecule A moves upward with a velocity w_A and

The average number of coins possessed per person is

$$\frac{64 \times 0 + 32 \times 1 + 16 \times 2 + 8 \times 3 + 4 \times 4 + 2 \times 5 + 1 \times 6}{64 + 32 + 16 + 8 + 4 + 2 + 1} = \frac{120}{127} = 0.945.$$

If one coin is taken from each person except the 64 who already have none, the distribution is

Number of coins (E) per person	0	1	2	3	4	5
" " persons possessing E coins	32	16	8	4	2	1

and the equation of this distribution is

$$32 \times 2^{-E} = 32 \times e^{-E\ln 2} = \underbrace{64 \times e^{-1\ln 2}}_{\text{Barometric formula}} \cdot \underbrace{e^{-E\ln 2}}_{\text{Energy distribution}}.$$

The average number of coins per person is now

$$\frac{32 \times 0 + 16 \times 1 + 8 \times 2 + 4 \times 3 + 2 \times 4 + 1 \times 5}{32 + 16 + 8 + 4 + 2 + 1} = \frac{57}{63} = 0.905.$$

The two figures for the average number of coins possessed per person (mean energy) do not agree exactly because the series is stopped after seven terms. If the next term be taken into account by giving half a person 7 coins in the first case and 6 in the second ("half a person" means one having 7 coins half the time and none for the remainder of the time, cf. p. 80), then the average possession of coins becomes in the first case 247/255 = 0.969 and in the second 120/127 = 0.945. The diagreement is thus decreased from 4.5 per cent to 2 per cent. *The essential point is therefore that the persons (molecules) already having no coins (zero energy) drop out entirely.*

[1] $\frac{dN}{NAdw}$ is plotted as ordinate against $0.43\,\frac{mw^2}{2kT}$ as abscissa.

molecule B moves downward with velocity w_B. If, however, these two collide, molecule A moves downward after the collision with velocity w_B and molecule B moves upward with velocity w_A. Since it does not matter which individual molecule (A or B) has a certain velocity and place, the collision has produced no change.

Finally, if horizontal velocity components are admitted, the vertical motion remains entirely unaffected. The magnitude and distribution of these horizontal components are readily deduced as follows: It has been pointed out that the distribution of velocities is independent of the strength of the gravitational field, and that the field merely brings the distribution to our attention. The distribution would remain unchanged, therefore, if there were no field in the vertical direction, but instead a constant field in the Y-direction. Then, just as before, in order that the temperature remain constant along the Y-axis at equilibrium, the velocity component η must be distributed according to the Maxwell Law

$$dN = N_0 A e^{-\frac{m\eta^2}{2kT}} d\eta. \tag{79}$$

A similar argument holds for ζ, the component in the Z-direction.

A More Exact Discussion of Maxwell's Law: Let us return again to the one dimensional gas. The number of molecules having velocities between ξ and $\xi + d\xi$ is

$$dN = A e^{-\frac{m\xi^2}{2kT}} d\xi. \tag{80}$$

The numerator and denominator of the exponent may each be multiplied by N_A giving

$$\frac{N_A m\xi^2}{2N_A kT} = \frac{M\xi^2}{2RT}. \tag{81}$$

This expression contains only quantities referring to one mol, therefore the distribution law cannot be used to calculate N_A. The constant A is evaluated from the fact that the total number of molecules present is N_0. That is

$$A \int_{-\infty}^{+\infty} e^{-\frac{m\xi^2}{2kT}} d\xi = N_0. \tag{81'}$$

The evaluation of this and similar integrals is best obtained by the change of variables

$$\frac{m\xi^2}{2kT} = x^2 \qquad \text{or} \qquad \xi\sqrt{\frac{m}{2kT}} = x. \tag{82}$$

This shows at once the manner in which m and T, the important quantities, enter A, leaving only a numerical factor to be calculated:

$$A\sqrt{\frac{2kT}{m}} \int_{-\infty}^{+\infty} e^{-x^2} dx = N_0, \tag{83}$$

$$A = N_0 \sqrt{\frac{m}{2\pi kT}}. \tag{84}$$

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If the distribution be represented graphically by plotting ξ as abscissa against the ordinate $\frac{1}{N_0}\frac{dN}{d\xi}$, a magnitude which gives the relative frequency of the different velocities, there is obtained a curve which, at $\xi = 0$, meets the ordinate $\sqrt{m/2\pi kT}$ with a horizontal tangent (Fig. 12, I). This horizontal tangent is caused by the presence of the square of ξ in the numerator of the exponent and would not appear if the energy, $m\xi^2/2$, were plotted as the abscissa. This

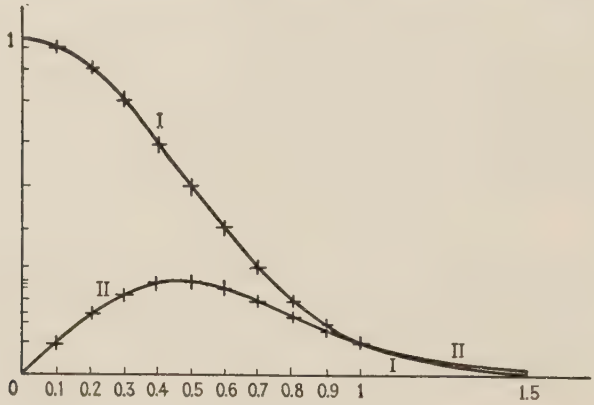

FIG. 12.

latter curve will lie below the former for small values of ξ and above the former for large values of ξ. (Fig. 12, II).

As ξ is increased (curve I) the ordinate decreases slowly at first and then much more rapidly.[1] The fraction of the molecules having velocities between ξ and $\xi + d\xi$ does not change greatly as long as $m\xi^2/2$ is of the order of magnitude of kT. On the other hand, if $m\xi^2/2 = 10kT$, the ordinate is only $e^{-10} = 10^{-4.3\cdots} = \frac{1}{2} \times 10^{-4}$ times its original value; if $m\xi^2/2 = 20kT$, $\frac{1}{4} \times 10^{-8}$, etc. The fraction of the molecules possessing an energy greater than some given value $m\xi_0^2/2$ is

$$\frac{N}{N_0} = \frac{\int_{\xi_0}^{\infty} e^{-\frac{m\xi^2}{2kT}} d\xi}{\int_0^{\infty} e^{-\frac{m\xi^2}{2kT}} d\xi} = 2\sqrt{\frac{1}{\pi}} \int_{\sqrt{m\xi_0^2/2kT}}^{\infty} e^{-x^2} dx = 1 - \Phi(x_0). \qquad (85)$$

The last integral (Φ = Gauss' error function) can only be evaluated as an infinite series. Its values have, however, been tabulated and may be found in B. O. Pierce, A Short Table of Integrals, Ginn and Co. (1910). The following extract suffices for small values of the lower limit, i.e. $\sqrt{\text{energy}/kT}$.

[1] It must be borne in mind that the discussion still deals with a one-dimensional gas.

TABLE I

Lower limit, x_0	Integral $(1 - \Phi(x_0))$
0	1
0.1	0.89
0.2	0.78
0.3	0.67
0.4	0.57
0.5	0.48
0.6	0.40
0.8	0.26
1	0.16
1.5	0.034
2	47×10^{-4}
3	22×10^{-6}
4	15×10^{-9}

The series from which the values are obtained are:

$$\left.\begin{aligned} &x < 1: \\ &\frac{2}{\sqrt{\pi}}\int_0^x e^{-x^2}\,dx = \frac{2}{\sqrt{\pi}}\left(x - \frac{x^3}{3} + \frac{1}{2!}\frac{x^5}{5} - \frac{1}{3!}\frac{x^7}{7} + \cdots\right) \\ &x > 1: \\ &\frac{2}{\sqrt{\pi}}\int_0^x e^{-x^2}\,dx = 1 - \frac{2e^{-x^2}}{\sqrt{\pi}}\left(\frac{1}{2x} - \frac{1}{4x^3} + \frac{3}{8}\frac{1}{x^5} - \frac{15}{16}\frac{1}{x^7} + \cdots\right). \end{aligned}\right\} \tag{86}$$

On account of the high rate of decrease of the curve at high values of ξ, the number of molecules having a velocity greater than a definite limit ξ_0 is practically the same as the number having velocities between ξ_0 and $\xi_1 > \xi_0$, provided that ξ_0 is sufficiently large and the interval ξ_0 to ξ_1 is not too small. This is due to the fact that the number of molecules having velocities greater than ξ_1 is relatively small.

The influence of a change of temperature upon the shape of the curve is deduced as follows: If, instead of the temperature T_1, the gas is maintained at some higher temperature, T_2, the velocity ξ_2 at which the exponent and therefore the exponential term have the value previously determined by ξ_1 and T_1 is given by

$$\frac{m\xi_1^2}{2kT_1} = \frac{m\xi_2^2}{2kT_2}. \tag{87}$$

Therefore $\xi_2 > \xi_1$ and the whole curve is extended in a horizontal direction by an amount proportional to the square roots of the temperatures. Since, however, the area included between the curve the abscissa and the ordinate must always be equal to unity,

$$\frac{1}{N_0}\int \frac{dN}{d\xi}\,d\xi = 1, \tag{88}$$

the ordinate A at $\xi = 0$ must be diminished by the factor $1/\sqrt{T}$ according

to equation (84). The effect is therefore to lessen the inequality of distribution of the velocities, the number of molecules with relatively large velocities being increased to the greater extent. The total number of molecules having an energy greater than some given value, for example, $10kT_1$ is the fraction 7.9×10^{-6} of all the molecules present. If the temperature is doubled, the energy value that has been assumed becomes $5kT_2$ and 1.5×10^{-3} of the molecules present now have an energy equal to or greater than this value.

On the other hand, the number of molecules having a relatively small energy is much less affected by changes in temperature. Thus, those molecules having an energy greater than $2kT$ form about 5 per cent of the total. Doubling the temperature increases this fraction to about 16 per cent.[1]

The mean kinetic energy is

$$\frac{\int \frac{m}{2}\xi^2 dN}{N_0} = \frac{\int_{-\infty}^{+\infty} \frac{m}{2}\xi^2 e^{-\frac{m\xi^2}{2kT}} d\xi}{\int_{-\infty}^{+\infty} e^{-\frac{m\xi^2}{2kT}} d\xi} = kT \frac{\int_{-\infty}^{+\infty} x^2 e^{-x^2} dx}{\int_{-\infty}^{+\infty} e^{-x^2} dx} = \frac{kT}{2}. \qquad (89)$$

The number of molecules which collide with 1 sq. cm. of the wall in one second is, according to equation (17),

$$\int \xi dN = \frac{N_0}{v} \frac{\int_0^{\infty} \xi e^{-\frac{m\xi^2}{2kT}} d\xi}{\int_{-\infty}^{+\infty} e^{-\frac{m\xi^2}{2kT}} d\xi} = \frac{N_0}{v}\sqrt{\frac{2kT}{m}} \frac{\int_0^{\infty} x e^{-x^2} dx}{\int_{-\infty}^{+\infty} e^{-x^2} dx} = \frac{N_0}{2v}\sqrt{\frac{2kT}{\pi m}}. \qquad (90)$$

If this is set equal to (17′), there is obtained

$$|\overline{w}| = 2\sqrt{\frac{2kT}{\pi m}} = 2\sqrt{\frac{2RT}{\pi M}}. \qquad (91)$$

[1] The distribution of a gas in a gravitational field is entirely analogous. Here, too, there is an exponential distribution of density upwards. At a sufficiently great height it becomes immaterial whether the calculations deal with the total quantity of gas above this height or the amount of gas in a sufficiently thick finite layer, since the quantity neglected by limiting the calculation to a layer is relatively very small. The corresponding air pressure is a measure of this neglected quantity and the previous statement amounts to saying that it is not very inaccurate to use the difference in pressure between the given high altitude and a still higher one, rather than the total atmospheric pressure at a given height.

The analogy may also be extended to the effect of temperature changes. Increase in temperature decreases the differences in density, because the decrease in the exponent of equation (58) lessens the influence of the exponential term or, speaking physically, because for a given density the pressure increases (equation (56)) and therefore a smaller *relative* change of pressure suffices to support an equal weight.

As in the Maxwell Law, the density at zero height must decrease on account of the increase of density in the upper levels, provided that the quantity of gas is constant. Formally, however, a gas in a gravitational field is analogous to a two-rather than a one-dimensional gas since the distribution is $e^{-\frac{mgx}{kT}} dx$ corresponding to equation (102) and not (80).

It should be noted that the average velocity $|\overline{w}|$ is connected with the square root of the average of the square of the velocity (root-mean square velocity $\sqrt{\overline{w^2}}$, equations (26) and (37)) by the relation

$$|\overline{w}| = 2\sqrt{\frac{2}{3\pi}}\sqrt{\overline{w^2}} = 0.922\sqrt{\overline{w^2}}. \tag{92}$$

The difference between these two quantities is due to the fact that they were obtained by different methods of averaging.[1] Although both are proportional to $\sqrt{RT/M}$, the proportionality constant differs according to the method used. This variety of proportionality constants, which occurs frequently in the deductions of the Kinetic Theory, will be discussed in detail below.

Upon proceeding to the case of a two dimensional gas it is to be remembered that, according to the conclusion reached on p. 99, the distribution of velocities along the X-axis is completely independent of the distribution along the Y-axis.

The number of molecules simultaneously satisfying the two conditions to the effect that the X components of their velocities lie between ξ and $\xi + d\xi$ and their Y components between η and $\eta + d\eta$,[2] may be expressed by

$$\frac{d_{\xi\eta}N}{N_0} = f(\xi, \eta)d\xi d\eta. \tag{93}$$

The uniform distribution of directions of velocities requires that the function f depends not on the individual values of ξ and η, but only on the magnitude of the total velocity. According to the parallelogram law the latter is $\sqrt{\xi^2+\eta^2}$. The function, therefore, has the form $f(\sqrt{\xi^2 + \eta^2})$. In order to evaluate this function it will be integrated over all possible values of η, ξ being held constant The expression resulting from this integration is simply the distribution law of the ξ components alone, equation (80). That is

$$\int_{-\infty}^{+\infty} f(\sqrt{\xi^2 + \eta^2})d\eta = Ae^{-\frac{m\xi^2}{2kT}}. \tag{94}$$

Upon solving this integral equation it is found that

$$f = \frac{m}{2\pi kT}e^{-\frac{m(\xi^2+\eta^2)}{2kT}} = \sqrt{\frac{m}{2\pi kT}}e^{-\frac{m\xi^2}{2kT}}\sqrt{\frac{m}{2\pi kT}}e^{-\frac{m\eta^2}{2kT}}, \tag{95}$$

which states that the fraction of the molecules having simultaneously x-components of velocity between ξ and $\xi + d\xi$ and Y components between η and $\eta + d\eta$ is obtained by multiplying the fraction of all the molecules present fulfilling the first condition by the fraction fulfilling the second. The validity

[1] Consider two molecules, one of the velocity 1, the other of the velocity 5, their average velocity is $|\overline{w}| = (1 + 5)/2 = 3$. The average of the square velocity is $\overline{w^2} = (1 + 25)/2 = 26/2$, $\sqrt{\overline{w^2}} = 3.6$.

[2] The variables of differentiation are written as subscripts after the sign of differentiation. More properly, d^2N should be used.

of such a proposition means that the components along the X-axis are completely independent of the components along the Y-axis. That is, a molecule with any definite X-component ξ, has no particular preference for any (especially large or especially small) Y component η. The same value for the *fraction* of molecules with X component between ξ and $\xi + d\xi$ is obtained whether it is calculated for all the molecules or only those having Y components between η and $\eta + d\eta$.

The first number is given by

$$\frac{d_\xi N}{N_0} = \sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{m\xi^2}{2kT}}\, d\xi \int_{-\infty}^{+\infty} \sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{m\eta^2}{2kT}}\, d\eta = \sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{m\xi^2}{2kT}}\, d\xi, \qquad (95)$$

and the second by

$$\left.\begin{aligned} \frac{d_{\xi\eta}N}{d_\eta N} &= \frac{\sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{m\xi^2}{2kT}} \sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{m\eta^2}{2kT}}\, d\xi d\eta}{\sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{m\eta^2}{2kT}}\, d\eta} \\ &= \sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{m\xi^2}{2kT}}\, d\xi. \end{aligned}\right\} \qquad (96)$$

The situation may be represented in a "$\xi - \eta$ plane," which is a plane described by the rectangular coordinates ξ and η (Fig. 13). Thus for each molecule there is a "state point" designated by the coordinates ξ and η which are the components of the velocity of the molecule represented. The radius vector from the origin to this state point represents the molecule's velocity both in magnitude ($\sqrt{\xi^2 + \eta^2}$) and direction. The number of state points in any elementary area $d\xi d\eta$ is given by equations (93) and (95), whence the density of state points at ξ, η is

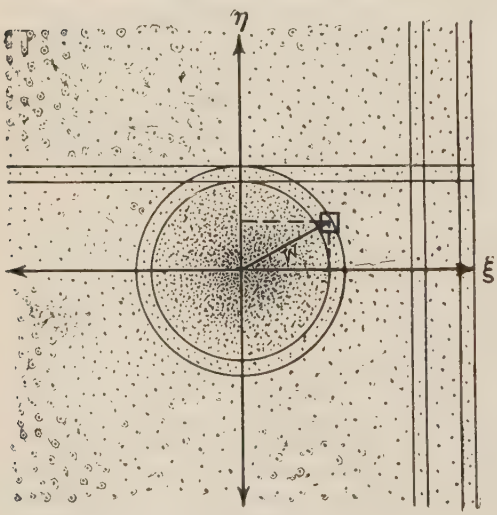

FIG. 13.

$$N_0 \frac{m}{2\pi kT} e^{-\frac{m}{2}\frac{\xi^2+\eta^2}{kT}}. \qquad (98)$$

The maximum density is at the origin where $w^2 = \xi^2 + \eta^2 = 0$. Going out from this point, the *density* decreases according to the laws which have been previously developed for a one dimensional gas. The leveling off of the density with increasing temperature is also similar to the previous case. In

agreement with the foregoing assumption, it is seen that the density in the figure depends only upon the magnitude of w and not upon its direction. It is therefore frequently convenient to express the velocity in the polar coordinates, w, the magnitude, and φ, the angle between the velocity and the positive X-axis. An elementary area then equals

$$dw.wd\varphi \tag{99}$$

and the number of points lying in this region is

$$N_0 \frac{m}{2\pi kT} e^{-\frac{mw^2}{2kT}} wdwd\varphi. \tag{100}$$

This is the number of molecules having velocities of magnitude between w and $w + dw$ and a direction making an angle between φ and $\varphi + d\varphi$ with the X axis. The number of molecules with velocities of magnitudes between the given limits regardless of direction, is

$$d_w N = N_0 \frac{m}{2\pi kT} e^{-\frac{mw^2}{2kT}} wdw \int_0^{+2\pi} d\varphi = N_0 \frac{m}{kT} e^{-\frac{mw^2}{2kT}} wdw. \tag{101}$$

This is the number of molecules whose state points lie within an annulus of inner radius w and width dw, accordingly, within the area $2\pi wdw$. Upon plotting the magnitude $d_w N/N_0 dw$ against w (Fig. 12, II) it is found to be zero when $w = 0$, and, as w increases, it rises to a maximum and then diminishes along a curve which, for large values of w, has again essentially an exponential decrease. The maximum is caused by the facts that the density continually decreases with increasing w, at first slowly and then quite rapidly, but the annular area increases linearly with w. At first, the uniform increase of the area is relatively larger than the slow decrease of the density. At large values of w the relative importance of the two terms is reversed.[1] The physical meaning of this increase of area with the increase in w is that large velocities may be compounded from a great many more combinations of the two components. Thus, for example, a large velocity may be compounded from a small ξ and a large η, a moderate ξ and a moderate η, or a large ξ and a small η. To summarize: Fig. 13 shows that a discussion of the distribution of the magnitudes of the velocities involves consideration of successive rings. It also shows that the distribution of X-components of velocity among that particular sub-group of molecules which have Y-components between η and $\eta + d\eta$ is given by the distribution along the horizontal strip between η and $\eta + d\eta$. It must be noted that this last *distribution* does not depend on the

[1] If the distribution had been plotted against energy instead of velocity writing

$$dN = N_0 \frac{1}{2\pi kT} e^{-\frac{mw^2}{2kT}} d\left(\frac{m}{2} w^2\right) \tag{102}$$

there would have been no maximum. The distribution of density over the energy axis decreases continually with increasing energy.

position η of the horizontal strip, just as in the case of a column of gas under the influence of gravity the relative distribution is independent of the density at the bottom of the column. Finally, the distribution of the X-component alone is found by comparing the total number of points contained in the various vertical strips.

The most probable velocity, i.e., the one for which $d_w N/dw$ has its maximum value, is given by

$$\frac{d}{dw}\left(e^{-\frac{mw^2}{2kT}}w\right) = 0; \quad \frac{mw_{mp}^{\ 2}}{2} = \frac{kT}{2}. \tag{103}$$

A calculation of the average energy of the molecules of this two dimensional gas gives the result:

$$\frac{m}{2}\overline{w^2} = \frac{\int_{-\infty}^{+\infty} \frac{m}{2} w^2 e^{-\frac{mw^2}{2kT}} w dw}{\int_{-\infty}^{+\infty} e^{-\frac{mw^2}{2kT}} w dw} = kT \frac{\int_{-\infty}^{+\infty} x^2 e^{-x^2} x dx}{\int_{-\infty}^{+\infty} e^{-x^2} x dx} = kT. \tag{104}$$

To proceed finally to a three dimensional gas, it will merely be necessary to generalize the results which have already been obtained. Thus the number of molecules whose velocities have X components between ξ and $\xi + d\xi$, Y components between η and $\eta + d\eta$, and Z components between ζ and $\zeta + d\zeta$, is given by

$$d_{\xi\eta\zeta}N = N_0 \sqrt{\frac{m}{2\pi kT}}^3 e^{-\frac{m}{2}\frac{(\xi^2+\eta^2+\zeta^2)}{kT}} d\xi d\eta d\zeta. \tag{105}$$

As in the discussion of the distribution of directions of velocities it is necessary to use the " velocity space " in order to give a graphical representation. In this space each molecule has a state point. The radius vector from the origin to this state point represents the velocity of the particular molecule in magnitude and direction. In the earlier discussion it was assumed that the directions of the velocities were uniformly distributed and that all the molecules moved with the same velocity, so that all the state points fell on the surface of a single sphere. Now, however, the state points will be distributed through space with a density equal to

$$N_0 \sqrt{\frac{m}{2\pi kT}}^3 e^{-\frac{mw^2}{2kT}}. \tag{106}$$

This density is greatest at the origin and decreases outward according to the much discussed exponential law. If a velocity is designated by its magnitude, w, and its direction ($\pi/2 - \vartheta$ = geographical latitude, φ = geographical longitude), instead of its components, ξ, η, ζ, the size of the volume element is

$$w^2 dw \sin\vartheta d\vartheta d\varphi. \tag{107}$$

Then the number of molecules having velocities of magnitude between w

and $w + dw$, and directions between ϑ and $\vartheta + d\vartheta$, and φ and $\varphi + d\varphi$, is given by

$$d_{w\vartheta\varphi} N = N_0 \sqrt{\frac{m}{2\pi kT}}^3 e^{-\frac{mw^2}{2kT}} w^2 dw \sin\vartheta d\vartheta d\varphi. \tag{108}$$

The number of molecules having speeds between w and $w + dw$, regardless of the direction of their motion, is the number whose state points lie within the spherical shell of internal diameter w and thickness dw. The state points are

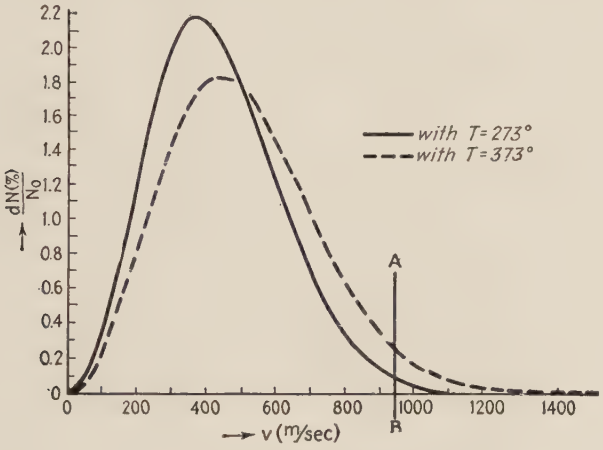

FIG. 14.

uniformly distributed in this shell and since its volume is $4\pi w^2 dw$, the desired number of molecules is (Fig. 14)

$$d_w N = 4\pi N_0 \sqrt{\frac{m}{2\pi kT}}^3 e^{-\frac{mw^2}{2kT}} w^2 dw. \tag{109}$$

This number is zero when w equals zero, and increases with increasing w to a maximum at

$$\frac{m}{2} w_{mp}^2 = kT.$$

Further increase in w causes a decrease in the fraction of the molecules with speed between w and $w + dw$, this decrease eventually approximating the type of a pure exponential decrease. The mathematical reason for the presence of the maximum is, as in the two dimensional case, that although the density of state points continually decreases upon moving away from the origin, the volume of the spherical shell continually increases. Physically the last statement means that large velocities may be formed from more combinations of components than small. This again merely corresponds to the geometrical statement that there are more volume elements in the large shell, for each

element of volume stands for a definite combination of the components ξ, η, ζ. The expression for the mean energy now takes the form

$$\frac{\overline{mw^2}}{2} = \frac{\int_0^{+\infty} \frac{m}{2} w^2 e^{-\frac{mw^2}{2kT}} w^2 dw}{\int_0^{+\infty} e^{-\frac{mw^2}{2kT}} w^2 dw} = kT \frac{\int_0^{+\infty} x^2 e^{-x^2} x^2 dx}{\int_0^{+\infty} e^{-x^2} x^2 dx} = \frac{3}{2} kT. \qquad (110)$$

The various values of $\overline{mw^2}/2$ obtained for the different models of gases assumed, may be summarized as follows:

One dimensional gas	$\frac{1}{2}kT$
Two " "	$\frac{2}{2}kT$
Three " "	$\frac{3}{2}kT$

It is seen from this table, as has already been deduced from the semi-empirical relation $U = 3RT/2$, that for each new direction of motion the average energy per molecule is increased by $kT/2$. Why this should be the case becomes obvious upon writing the equation in rectangular rather than in polar coordinates. It then becomes

$$\left.\begin{aligned}\frac{\overline{m}}{2} w^2 = &\frac{\int_{-\infty}^{+\infty} \frac{m}{2} \xi^2 e^{-\frac{m\xi^2}{2kT}} d\xi \int_{-\infty}^{+\infty} e^{-\frac{m\eta^2}{2kT}} d\eta \int_{-\infty}^{+\infty} e^{-\frac{m\zeta^2}{2kT}} d\zeta}{\int_{-\infty}^{+\infty} e^{-\frac{m\xi^2}{2kT}} d\xi \int_{-\infty}^{+\infty} e^{-\frac{m\eta^2}{2kT}} d\eta \int_{-\infty}^{+\infty} e^{-\frac{m\zeta^2}{2kT}} d\zeta} \\ &+ \frac{\int_{-\infty}^{+\infty} e^{-\frac{m\xi^2}{2kT}} d\xi \int_{-\infty}^{+\infty} \frac{m}{2} \eta^2 e^{-\frac{m\eta^2}{2kT}} d\eta \int_{-\infty}^{+\infty} e^{-\frac{m\zeta^2}{2kT}} d\zeta}{\int_{-\infty}^{+\infty} e^{-\frac{m\xi^2}{2kT}} d\xi \int_{-\infty}^{+\infty} e^{-\frac{m\eta^2}{2kT}} d\eta \int_{-\infty}^{+\infty} e^{-\frac{m\zeta^2}{2kT}} d\zeta} \\ &+ \frac{\int_{-\infty}^{+\infty} e^{-\frac{m\xi^2}{2kT}} d\xi \int_{-\infty}^{+\infty} e^{-\frac{m\eta^2}{2kT}} d\eta \int_{-\infty}^{+\infty} \frac{m\zeta^2}{2} e^{-\frac{m\zeta^2}{2kT}} d\zeta}{\int_{-\infty}^{+\infty} e^{-\frac{m\xi^2}{2kT}} d\xi \int_{-\infty}^{+\infty} e^{-\frac{m\eta^2}{2kT}} d\eta \int_{-\infty}^{+\infty} e^{-\frac{m\zeta^2}{2kT}} d\zeta}.\end{aligned}\right\} \qquad (111)$$

from which the values of the individual summands are directly obtainable.

It is now possible to prove the assumption that gases of different molecular weight in thermal equilibrium have the same kinetic energy (p. 87). The above deduction of the Maxwell Law has been carried through for the case of a single gas. However, as a review of the deductions of the foregoing paragraphs will show, the only use that has been made of this limitation, has been the fact that the pV product is constant throughout the entire column of gas. Although the right hand side of $pV = 2U_k/3$ has been written equal to $N_A kT$, no use has been made of this relation, since in all of the formulae of this and the preceding sections the quantity $\frac{2}{3}\frac{m}{2}\overline{w^2}$ could be substituted for kT. It

will now be shown that in a mixture of gases where the separate components obey the distribution laws

$$dN_1 = N_{01}\sqrt{\frac{3}{2\pi\overline{w_1^2}}}^3 e^{-\frac{3}{2}\frac{\xi_1^2+\eta_1^2+\zeta_1^2}{\overline{w_1^2}}} d\xi_1 d\eta_1 d\zeta_1 \tag{112}$$

and

$$dN_2 = N_{02}\sqrt{\frac{3}{2\pi\overline{w_2^2}}}^3 e^{-\frac{3}{2}\frac{\xi_2^2+\eta_2^2+\zeta_2^2}{\overline{w_2^2}}} d\xi_2 d\eta_2 d\zeta_2 \tag{113}$$

the kinetic energies of the constituents are equalized as a result of collisions.

In order to do this it is first necessary to investigate the distribution of the relative velocities [1] since it is this alone which determines the number and kind of collisions. Consider two molecules with velocities ξ_1, η_1, ζ_1, and ξ_2, η_2, ζ_2. Their relative velocity is

$$\tilde{w} = \sqrt{(\xi_1 - \xi_2)^2 + (\eta_1 - \eta_2)^2 + (\zeta_1 - \zeta_2)^2}, \tag{114}$$

the components of this relative velocity being

$$\tilde{w}_x = \xi_1 - \xi_2 \qquad \tilde{w}_y = \eta_1 - \eta_2 \qquad \tilde{w}_z = \zeta_1 - \zeta_2. \tag{115}$$

The relative velocity is, from the geometry of the velocity space, the vector drawn from the state point of molecule I to that of molecule II. It is, accordingly, the vector difference of two velocities

$$\tilde{w} = w_1 - w_2. \tag{116}$$

The relation is identical with the former expression.

The fraction of the total number of pairs having prescribed velocities is

$$\begin{aligned}\frac{dN_1}{N_{01}}\cdot\frac{dN_2}{N_{02}} &= \sqrt{\frac{3}{2\pi\overline{w_1^2}}}^3\sqrt{\frac{3}{2\pi\overline{w_2^2}}}^3 e^{-\frac{3}{2}\frac{\xi_1^2+\eta_1^2+\zeta_1^2}{\overline{w_1^2}}-\frac{3}{2}\frac{\xi_2^2+\eta_2^2+\zeta_2^2}{\overline{w_2^2}}} \\ &\qquad \times d\xi_1 d\eta_1 d\zeta_1 d\xi_2 d\eta_2 d\zeta_2 \\ &= \sqrt{\frac{3}{2\pi\overline{w_1^2}}}^3\sqrt{\frac{3}{2\pi\overline{w_2^2}}}^3 e^{-\frac{3}{2}\frac{\xi_1^2+\eta_1^2+\zeta_1^2}{\overline{w_1^2}}-\frac{3}{2}\frac{(\xi_1-\tilde{w}_x)^2+(\eta_1-\tilde{w}_y)^2+(\zeta_1-\tilde{w}_z)^2}{\overline{w_2^2}}} \\ &\qquad \times d\xi_1 d\eta_1 d\zeta_1 d\tilde{w}_x d\tilde{w}_y d\tilde{w}_z.\end{aligned} \tag{117}$$

The fraction of pairs having relative velocities with components between $\tilde{w}_x$ and $\tilde{w}_x + d\tilde{w}_x$, etc., regardless of the individual values of ξ_1, η_1, ζ_1, is obtained upon integration of the above relation with respect to ξ_1, η_1, ζ_1, from $-\infty$ to $+\infty$,

$$\left.\begin{aligned}\frac{d\tilde{w}(N_1N_2)}{N_{01}N_{02}} &= \sqrt{\frac{3}{2\pi(\overline{w_1^2}+\overline{w_2^2})}}^3 e^{-\frac{3}{2}\frac{\tilde{w}_x^2+\tilde{w}_y^2+\tilde{w}_z^2}{(\overline{w_1^2}+\overline{w_2^2})}} d\tilde{w}_x d\tilde{w}_y d\tilde{w}_z \\ &= \sqrt{\frac{3}{2\pi(\overline{w_1^2}+\overline{w_2^2})}}^3 e^{-\frac{3}{2}\frac{\tilde{w}^2}{\overline{w_1^2}+\overline{w_2^2}}} d\tilde{w}_x d\tilde{w}_y d\tilde{w}_z,\end{aligned}\right\} \tag{118}$$

[1] Clerk Maxwell, *Phil. Mag.*, **25** (1860); *Scient. Papers*, **1**, 382.

and the average value of $\tilde{w}^2$ is [1]

$$\overline{\tilde{w}^2} = \overline{w_1^2} + \overline{w_2^2} \tag{119}$$

But this result would be obtained if the velocities of the molecules of types I and II were perpendicular (Law of Pythagoras applied to the addition of vectors). Therefore, the average angle between w_1 and w_2 may be taken to be 90°.

The average difference of the kinetic energies of the molecules after collision is obtained by squaring and subtracting the formulas given on page 16 (the energy due to the components of velocity perpendicular to the line of centers, which are not affected by the collisions is added to the result).

$$\frac{m_1\overline{w_1^2}}{2} - \frac{m_2\overline{w_2^2}}{2} = \left(1 - \frac{8m_1m_2}{(m_1+m_2)^2}\right)\left(\frac{m_1\overline{w_1{}^{0^2}}}{2} - \frac{m_2\overline{w_2{}^{0^2}}}{2}\right) + 4\frac{m_1m_2(m_1-m_2)}{(m_1+m_2)^2}\overline{w_{1z}{}^0 w_{2z}{}^0}. \tag{120}$$

Now the average value of the product of the components along a given line (in this case the line of centers) vanishes if, on the average, the velocities are perpendicular to each other. Therefore, the last term of the above relation is zero. Since the first parenthesis is less than unity, the energy difference between the two molecules after collision is less than it was before collision. In a mixture of gases, therefore, the energies of the constituents are equalized. From this it may be concluded that when gases are placed in contact their energies finally become equal and it follows from this that the kinetic energies of all gases must be the same function of the temperature. Here again merely the constancy of the pV product in the column has been stipulated.

The Experimental Proof of Maxwell's Law: [2] Qualitatively, Maxwell's Law states that the molecules of a gas do not all move with the same speed and that an increase in the temperature of the gas causes an increase in the number of molecules possessing high speeds. Quantitatively, the law specifies the exact form of the distribution curve at each temperature.

On the experimental side, the distribution of a gas in a field of force shows that all molecules do not possess the same speed, since, according to the barometric formula, the molecules are sorted out by the gravitational field into a kind of velocity spectrum. Similarly, the laws of vapor pressure may be cited as proof of the distribution law in this way: In order to pass from the liquid to the vapor phase a molecule must have sufficient velocity to overcome the attractive forces holding the liquid together. These forces are evidenced by the latent heat of evaporation which is analogous to the potential energy,

[1] This follows from a direct calculation in which each value of

$$\tilde{w}^2 = \tilde{w}_x{}^2 + \tilde{w}_y{}^2 + \tilde{w}_z{}^2$$

is multiplied by the frequency of its occurrence.

[2] Cf. J. F. Andrews, *Science Progress*, **23**, 118 (1928).

mgx, appearing in the barometric formula. If all the molecules of a liquid had the same velocity, none could evaporate at low temperatures. If the temperature of such a liquid were increased a point would finally be reached at which the liquid would suddenly vaporize. This temperature would be independent of the pressure; above it, the substance could exist only as a gas and below it only as a liquid or solid with zero vapor pressure. The experimental fact that liquids and solids can evaporate at all temperatures shows that some of the condensed molecules must have sufficient velocity to escape into the vapor phase. Further, the fact that the vapor pressure increases with the temperature shows that increase in temperature increases the number of high speed molecules. It will be seen later that the exact form of the vapor pressure-temperature curve is determined by Maxwell's Law.

A study of the width of spectral lines gives further evidence for the statements of the distribution law. It may be assumed that the light emitted from a radiating atom is very nearly monochromatic. The light emitted from a large number of atoms, however, will not be monochromatic due to the motion of the emitting atoms (Doppler effect). Thus, if at the instant of emission the atom is moving toward the observer, the apparent wave length is slightly less than that emitted by a stationary atom. The different motions of the emitting atoms therefore cause a slight broadening of the line as observed by spectroscopic measurements. It has been shown [1] that the experimental facts are in agreement with the predictions of Maxwell's Law.

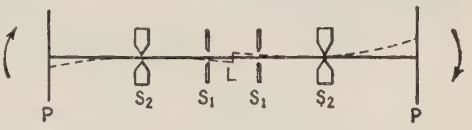

Fig. 15.

The first direct measurement of molecular velocities was obtained by Stern.[2] His apparatus is shown diagrammatically in Fig. 15. L represents a thin platinum wire shown end on in the figure. This wire is coated with silver which, upon heating to 600–700° C. evaporates, the silver atoms moving off radially from the wire in the plane of the figure. The apparatus is evacuated to such a degree that the collisions between the silver atoms are negligible. Therefore the atoms move in straight lines from the wire. S_1 and S_2 are slits which select a ray of silver atoms of a particular direction among all evaporating from the wire. The ray of atoms after passing through the slits is condensed on the receiver P in the form of a narrow strip, just as a light source placed at L would produce a fine band on a photographic plate at P. In order to measure the speed of the silver atoms the whole apparatus is rotated about L as an axis. The silver atoms may now be regarded as being shot from the stationary wire at a moving target, since the linear velocity of the periphery of the wire L is small compared to that of the plate P. The atoms will therefore deposit on the plate at a point slightly behind the previous point as

[1] Rayleigh, *Phil. Mag.*, [5], **27**, 298 (1889); A. A. Michelson, *ibid.*, **34**, 280 (1892) Buisson and Fabry, *J. phys.*, [5], **2**, 442 (1912).

[2] O. Stern, *Z. Physik*, **2**, 49 (1920); **3**, 417, (1920).

shown by the dotted line of the diagram. In the actual experiment Stern rotated the apparatus first in one direction and then in the other, obtaining two lines each deflected from the center by the same amount but in opposite directions (Fig. 16). From this displacement, the speed of rotation and the dimensions of the apparatus, the average velocity of the silver atoms was calculated to be from 643 to 675 m/sec. The value to be expected from the theory was 672 m/sec.

Fig. 16.

Costa, Smyth and Compton[1] have attempted a direct experimental proof of the quantitative statement of Maxwell's Law. The essential parts of their apparatus are shown in Fig. 17. S_1 and S_2 are slits used to define a beam of molecules (see p. 167). D_1 and D_2 are discs slotted at the rim in the manner of cog-wheels. These discs are mounted on the common axis A in such a manner that they can be rotated at a high speed (500–6000 R.p.m.), the slots in D_1 and D_2 being exactly in line. At R is placed a sensitive radiometer which, by its angular deflection, measures the intensity or number of molecules of the beam. The whole apparatus is placed in a highly evacuated chamber. If an experiment is made with the discs stationary and in such a position that one of the slots is opposite the slits, the radiometer deflection is a measure of the total number of molecules leaving slit S_1 in the direction of S_2, since there is no obstruction offered to their motion. In the actual measurements the discs are rapidly rotated in order

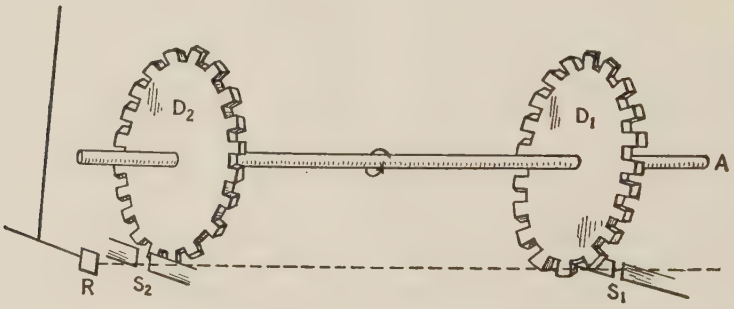

Fig. 17.

to sort out the molecules possessing a given speed. The mechanism of the separation is as follows. Consider a molecule leaving the slit S_1 with velocity w and passing through a slot in D_1. It can only pass through a slot in D_2 and be recorded by the radiometer if the time required for the traversal of the dis-

[1] J. L. Costa, H. D. Smyth and K. T. Compton, *Phys. Rev.*, **30**, 349 (1927).

tance between the discs equals some multiple of the time required for D_2 to turn over until the next slot is in the path of the beam. That is if

$$\frac{d}{w} = n\frac{2\pi r}{a}\cdot\frac{1}{r\omega} \qquad \text{or} \qquad nw = \frac{ad\omega}{2\pi}, \tag{121}$$

where r is the radius of the discs, d the distance between them, a the number of slots in each disc, ω the angular velocity of the discs and n a small integer. The deflection of the radiometer at a rotatory speed ω is therefore a measure of the number of molecules in the beam with a velocity approximately equal to w or some multiple thereof. Thus, the function of the discs is analogous to that of a grating in spectroscopy in that they separate the molecules into a velocity spectrum. The lack of definition of the speeds of the selected molecules is caused by the finite width of the slots. The multiplicity of the selected velocities is analogous to the second and higher orders of spectra obtained from a grating. Thus, all the molecules passing through a given slot in D_1 will miss the opposite slot in D_2 due to the rotation of the discs. Those molecules, however, which have a speed $w = ad\omega/2\pi$ $(n = 1)$ will pass through the next slot in D_2; those molecules having a speed $2w = 2(ad\omega/2\pi)$ $(n = 2)$ will pass through the third slot in D_2 counted from the slot opposite the one in D_1 through which the molecules entered.

Experiments were made with hydrogen, nitrogen and carbon tetrachloride. In Fig. 18 the radiometer deflection is plotted against the angular velocity of the discs. The solid lines are the results obtained by experiment and the dotted curves show the effect calculated from Maxwell's Law. Although the experimental results follow the general shape of the calculated curve, it is apparent that the check is not as good as might be desired. The experimental error, however, is large enough to account for the deviations from the theoretical values.

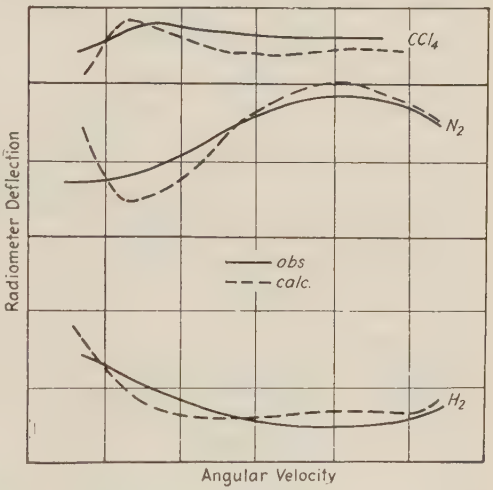

Fig. 18.

A similar experiment has been performed by Eldridge [1] using a beam of cadmium atoms. He also checked Maxwell's Law to within his experimental error.[2]

The application of Maxwell's Law to the rotational energy of diatomic molecules is readily tested by a study of the band spectra of such molecules.

[1] J. A. Eldridge, *Phys. Rev.*, **30**, 931 (1927).

[2] Cf. also Tykocinski-Tykociner, *J. Opt. Soc. Am.*, **14**, 423 (1927).

As will be proven below, the law is applicable to this case in the form (101) since there are two rotational degrees of freedom. If the axis of the molecule is supposed to lie for the moment along the Z-axis, rotation can take place about the X- or about the Y-axes, but not about the Z-axis since this would correspond merely to a rotation of the atoms about their respective centers of gravity, cf. p. 141. If the electrical charges in the molecules are not exactly symmetrical, light of frequency ν (which happens to lie in the infra-red) will be absorbed or emitted by those molecules which are rotating with exactly the same angular frequency.[1] Since, furthermore, both atoms vibrate with respect to each other with a frequency ν_0, the frequency absorbed by a molecule rotating with the angular frequency ν is $\nu' = \nu_0 + \nu$. The kinetic energy of rotation is

$$\frac{mw^2}{2} = \frac{I}{2} 4\pi^2 \nu^2,$$

where I is the moment of inertia of the molecule. The number of molecules whose angular frequency falls between ν and $\nu + d\nu$ is therefore proportional to

$$e^{-\frac{I4\pi^2}{2kT}\nu^2} \nu d\nu = e^{-\frac{I4\pi^2}{2kT}(\nu' - \nu_0)^2} (\nu' - \nu_0) d\nu' \qquad (122)$$

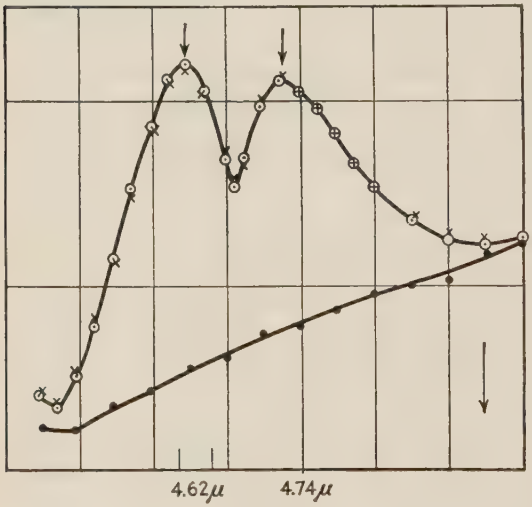

Fig. 19.

and since the quantity of light absorbed is approximately proportional to the number of absorbing molecules, the intensity of the band obeys this law approximately. The curve obtained by plotting intensity against frequency is symmetrical about the point $\nu' = \nu_0$, with a minimum at the center and maxima at $4\pi^2 I (\nu' - \nu_0)^2 = kT$. The moment of inertia of the molecule may therefore be determined from the curve. The curve of such a band for carbon monoxide is shown in Fig. 19.[2] The asymmetry is to be ascribed partly to a reciprocal effect of rotation and vibration, and partly to the fact that the absorption coefficient might *depend slightly* on ν.

A beam of electrically charged particles is much simpler to produce and measure than a beam of neutral molecules. It has therefore been possible to

[1] This statement is not quite correct from the point of view of the quantum theory. See Chapter XVI.

[2] E. v. Bahr, *Verh. deut. physik. Ges.*, **15**, 720 (1913).

confirm Maxwell's Law for electrons and positive ions with much greater accuracy than was obtained in the experiments outlined above. Richardson [1] and his coworkers have shown that the velocities of the electrons and positive ions emitted from hot bodies are distributed according to Maxwell's Law at the temperature of the emitting body. More recently Langmuir [2] has shown that the electrons and positive ions present in a uniformly ionized gas and in certain parts of the vacuum discharge are subject to the Maxwellian distribution.

One of the first experiments to show directly that the molecules of a gas possess high velocities is due to Cantor.[3] If one side of a copper plate is protected with glass and the whole hung in an atmosphere of chlorine, the side covered with glass experiences the full pressure $p = RT/V$. The pressure on the exposed side is smaller because some of the molecules of chlorine which form a solid compound with copper do not rebound elastically and therefore the momentum imparted by each of these molecules is only mw instead of $2mw$ (p. 76). This side therefore receives less than the normal amount of momentum. The excess pressure can readily be measured by mounting two such plates as vanes on an axis. From this value and the increase in the weight of the plate it is possible to calculate the number of molecules which do not rebound and their average momentum (velocity). Assuming that a molecule must have a minimum velocity to combine with the copper, the determination of the way in which the quantities mentioned above vary with temperature would lead to an experimental determination of the distribution law.[4]

A model of the molecular motion in gases which is suitable for educational purposes has been developed by Minneart. [5]

A piece of plane plate glass 70 cm. square is laid flat on a table. The molecules are represented by steel ball bearings about 8 mm. in diameter, and their motion is limited by a frame 40 cm. square made of wood about 2 cm. thick, the frame taking the part of the walls of the containing vessel. If the frame is now moved across the glass plate so that each point describes a circle about 6 cm. in diameter, the balls are set in motion and exchange the motion by collisions until a steady state is reached. In this case the motion of the frame corresponds to collisions of the molecules with a hot containing wall. The free path and number of collisions per second (see below) can be estimated in this manner and it can be observed how each ball moves in all directions in course of time and also changes the magnitude of its velocity. Moreover, the irregular nature of the path can be followed. In order to follow the course

[1] O. W. Richardson, The Emission of Electricity from Hot Bodies, Longmans Green and Co., 1921, p. 154 ff. and p. 206 ff.

[2] I. Langmuir, *Z. Physik*, **46**, 271 (1927).

[3] M. Cantor, *Wied. Ann.*, **62**, 482 (1897).

[4] A. Predovoditelev, *Z. Physik*, **46**, 406 (1927); cf. also L. Frommer and M. Polanyi, *Z. physik Chem.*, **137A**, 201 (1928).

[5] M. Minneart, *Z. physik. chem. Unterricht*, **32**, 69 (1919). Improvement by T. Wulf, *ibid.*, **34**, 5 (1921).

of a single ball, it is desirable to have one of the same mass but of different color, as for example, brass. If a smaller steel ball is added, it is seen to have a much greater velocity than the others.

If one side of the glass plate is blocked up higher than the other, the movement of the frame produces a barometric distribution of the balls since most of them stay in the lower portion although some are being continually thrown back into the upper region. If a mixture of balls of different weight is used the lighter ones are seen to spend more time in the upper part. A contrivance may be made out of a wooden border and tin strips which, when suddenly put into the frame while the balls are in motion, will separate them into horizontal strips. The distribution may then be counted. Furthermore, the interior of the frame may be divided into two parts, one of which contains large balls, the other small. If there is a hole in the dividing wall about 3 cm. across (the top of the wall being held together by a tin strip), the process of diffusion may be illustrated (p. 209).

Extension of Maxwell's Law to the Maxwell-Boltzmann Law: Conversely to the procedure of p. 93 ff., the distribution in space of a gas in a field of force which is independent of the time and which has a potential, can be deduced from the law governing the distribution of velocities. A reference point is arbitrarily selected in the space to be considered and the symbol ϵ_p is used to designate the work required to move a molecule from the reference point to any given point in the field. That is, the potential at the given point is calculated by arbitrarily setting the potential at the reference point equal to zero. Let N_0 be the number of molecules per cubic centimeter at the reference point. Then the " Maxwell-Boltzmann Distribution," [1]

$$dN = N_0 \sqrt{\frac{m}{2\pi kT}}^3 e^{-\frac{\left(\epsilon_p + \frac{m}{2}\xi^2 + \frac{m}{2}\eta^2 + \frac{m}{2}\zeta^2\right)}{kT}} d\xi d\eta d\zeta, \qquad (123)$$

obtains at the given point. This relation states that the Maxwell distribution of velocities (and also the isotropic distribution of directions of velocities) holds at every point in the space but that the total density of the molecules at the point is to be taken as

$$N = N_0 e^{-\frac{\epsilon_p}{kT}}. \qquad (124)$$

The content of formula (123) may also be expressed by the statement that the exponent is proportional to the sum of the potential (ϵ_p) and kinetic

$$\left(\frac{m}{2}\xi^2 + \frac{m}{2}\eta^2 + \frac{m}{2}\zeta^2\right)$$

energies instead of to the kinetic energy alone as was formerly the case.

This formula is valid for all fields of force, even those in which the change in the potential is large upon traversing a distance of the order of magnitude of the molecular diameter.[2]

[1] L. Boltzmann, *Wien. Ber.*, **58**, 517 (1868); **63**, 397 (1871).
[2] G. Jäger, *Wien. Ber.*, **112**, 307 (1903); **113**, 1289 (1904).

The derivation is merely the reverse of the process used on p. 93 ff. As an especially simple example consider a vessel separated into two parts by a dividing wall. No forces act within the two halves of the vessel, but in order to carry a molecule from left to right through the wall, a definite amount of work, ϵ_p is required. For instance, the molecules may be supposed to be electrically charged and the dividing wall to consist of two wire gauzes close together and connected to form a condenser. The same temperature and distribution of velocities then prevails on each side of the dividing wall. On the left hand side, however, the density is greater than that on the right by an amount given by the relation

$$c_r = c_l e^{-\frac{\epsilon_p}{kT}}. \tag{125}$$

Without going into particulars, this formula, as well as the fact of temperature constancy can be deduced, according to Jäger, merely from the condition that, in the stationary state, as many molecules pass across from left to right as in the opposite direction, and that the net heat exchange across the wall is zero.

FIG. 20.

There is still in this argument an apparent difficulty which has also been explained by Jäger. Consider a vessel separated into three parts by two dividing walls of the kind described above (Fig. 20). Then an amount of work equal to ϵ_p must be done on a molecule to transport it from II to either I or III. Consider now a molecule in I with an X-component of velocity equal to ξ, the X-axis being taken from I to II perpendicular to the dividing wall. Upon crossing the left wall ξ is increased according to the equation

$$\frac{m}{2}\xi_{II}^2 = \frac{m}{2}\xi_I^2 + \epsilon_p. \tag{126}$$

It traverses II with this higher velocity but, upon passing the right hand wall, it loses kinetic energy to the amount ϵ_p, since this energy must be given up as work to effect the passage. It then moves in compartment III with its original velocity:

$$\frac{m}{2}\xi_{III}^2 = \frac{m}{2}\xi_{II}^2 - \epsilon_p = \frac{m}{2}\xi_I^2. \tag{127}$$

From this it might be argued that since the molecule has a greater velocity in II than in either I or III, the *density* in II must be *less* than in I and III because the molecule requires less time to traverse a given path in II than in either I or III and hence in II it does not remain as long in a given volume as it does in the same volume of I and III. A similar effect is noticed when men walking single file start to run upon passing some fixed point; the distance between the running men is greater than that between the men who are still walking.

On the other hand, the Boltzmann Law requires that the *density* be *greatest* in compartment II.

The explanation of this apparent contradiction results upon taking into account those molecules which lose so much energy by collisions in II that

$$\frac{m}{2}\xi_{II}^2 < \epsilon_p. \tag{128}$$

These molecules have not enough energy to effect a passage through either of the dividing walls, for upon colliding with either of them they will penetrate to a certain depth and then be returned into II. They are then "reflected" back and forth between the two dividing walls and accordingly spend a large proportion of their time in compartment II. They cannot get out of this compartment until some collision has given them sufficient energy to make the passage. Even then they can get out only if they do not lose the energy again in another collision before reaching the dividing wall.

This retention of molecules in II is therefore the cause of the greater density existing in II, although, from the previous discussion, the density of those which pass completely through compartment II with unchanged velocity is smaller than the density in I and III. It must be particularly noted, however, that the density of this single class of molecules is greater by the factor $e^{\frac{\epsilon_p}{kT}}$ than the density of molecules of *equal* kinetic energy in compartments I and III. Those molecules which are retained in II due to a loss of energy by collision have small velocities, $\frac{m}{2}\xi_{II}^2 < \epsilon_p$, while the molecules which have just entered this compartment have a component of velocity in the X-direction $\frac{m}{2}\xi_{II}^2 > \epsilon_p$. Both of these classes of molecules participate in the Maxwell distribution which must prevail throughout the gas; that is, the retained molecules contribute the slow velocities and the entering molecules the high velocities with the result that, taken as a whole, the distribution of velocities is represented by Maxwell's Law.

The Number of Collisions; The Mean Free Path: (*a*) *Preliminary Treatment:* Up to this point the occurrence of collisions has been used to demonstrate the equalization of velocities but, as yet, nothing has been said in regard to the number of the collisions. To evaluate this quantity it will first be assumed that the molecules are rigid spheres which are without influence upon each other except at the instant of collision. It is further postulated that the gas is sufficiently attenuated to permit the assumption that during the collision of two molecules the chance of a third molecule being close enough to affect the process of collision is negligibly small. Consider a mixture of two gases which have the molecular diameters d_1 and d_2. A collision between two different molecules results if their centers approach to within a distance $(d_1 + d_2)/2$, corresponding to contact of their spherical surfaces (Fig. 21).

This may also be expressed by supposing spheres of radius $(d_1 + d_2)/2$ circumscribed about the molecules of the first kind and stating that a collision takes place when the center of a molecule of the second kind touches one of these spheres. Following Clausius'[1] treatment, the problem will be simplified by assuming that all the molecules of type I are held stationary and that there is only a single molecule of the type II present. This molecule is permitted to move with the velocity w. It is now necessary to determine the probability that this molecule will collide with one of the stationary molecules while traversing the interval Δx. Consider a cylinder with base equal 1 sq. cm. and altitude Δx. There are $N_1\Delta x$ molecules of Type I in this cylinder, where N_1 denotes the number of molecules of type 1 per cc. The single molecule of type II is now supposed to move toward the base of this cylinder, which offers to the molecule a surface of 1 sq. cm., part of which, however, is covered by $N_1\Delta x$ spheres of radius $(d_1 + d_2)/2$ circumscribed about the molecules of Type I. The covered portion of the surface equals $N_1\Delta x\pi(d_1 + d_2/2)^2$. If, upon traversing the cylinder, the center of the moving molecule comes in contact with this covered portion, a collision has taken place, but if, throughout the passage through the cylinder, the center of this molecule never falls within the spheres surrounding the molecules of type I, molecule II crosses the interval Δx undisturbed. It is essential for the validity of the following reasoning that the moving molecule is not "aiming for" any other molecule. That is to say, the particular point on the base of the cylinder toward which the molecule moves must depend only on the situation at the point from which the molecule started and not upon whether or not there is a molecule of type I located at the spot on the base of the cylinder which molecule II will strike.

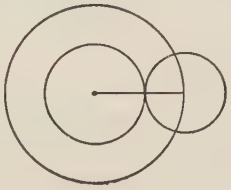

FIG. 21.

The problem is now entirely analogous to the following: A marksman shoots a number of shots toward a target without taking aim. Since, on the average, the bullets that hit the target will be uniformly distributed throughout its area, the fraction of bullets hitting the bulls-eye will equal the fraction of the total area of the target occupied by the bull's-eye.

Similiarly, to return to the problem in hand, the probability that the moving molecule will collide with a stationary one is

$$N_1\pi\left(\frac{d_1 + d_2}{2}\right)^2\Delta x \text{ or } \frac{\Delta x}{\Lambda}, \tag{129}$$

where the "mean free path," Λ, is defined by the equation

$$\Lambda = \frac{1}{N_1\pi\left(\frac{d_1 + d_2}{2}\right)^2} \tag{130}$$

[1] R. Clausius, *Pogg. Ann.*, **105**, 239 (1858).

or, in the case of a single gas,

$$\Lambda = \frac{1}{N\pi d^2}. \tag{131}$$

Thus, in a layer of thickness Λ and surface 1 sq. cm., the " absorbing area " (Lenard), i.e., the sum of the surfaces presented to the moving molecule disregarding the effect of overlapping, is equal to

$$\Lambda N_1 \pi \left(\frac{d_1 + d_2}{2}\right)^2 = 1 \text{ sq. cm.} \tag{132}$$

In other words, aside from overlapping, the area in a layer of thickness Λ appears to the moving molecule as if it were completely covered.

The choice of the name of " mean free path " for this interval will be made evident by the following considerations.

Suppose a ray of molecules of type II, all having approximately the same direction of motion and equal velocities, is shot into gas I. Then more and more of the molecules II will collide with molecules I and be deflected from the path of the ray. The probability that a molecule will experience a collision upon moving over the distance dx, is, from the above, dx/Λ. The fraction of the molecules which are deflected from the ray during this interval is accordingly

$$-\frac{dN_2}{N_2} = +\frac{dx}{\Lambda}. \tag{133}$$

Upon integration this gives the number of molecules still present in the ray after passing over the length of path x:

$$N_2 = N_{02}e^{-x/\Lambda}. \tag{134}$$

Therefore, this number of molecules decreases in a geometric progression. Hence the probability that a molecule can move over the distance x without taking part in a collision is

$$e^{-x/\Lambda} \tag{135}$$

and is thereby independent of the point at which the last collision has taken place, since it has not been assumed in the deduction that the point $x = 0$ must coincide with the point of the last collision, $x = 0$ being an arbitrarily selected point.[1] The mean value of the distance through which a molecule moves without colliding is given by

$$\int_0^\infty \frac{xe^{-x/\Lambda}dx}{e^{-x/\Lambda}dx} = \Lambda, \tag{136}$$

from which follows the name of mean free path.

The probability that a molecule will collide at least once, on traversing

[1] For the explanation of a misunderstanding in this connection see R. Clausius, *Wied. Ann.*, **10**, 92 (1880), and Mech. Wärmetheorie, III, Braunschweig, 1891, p. 204.

the distance x is proportional to the number of molecules present and to [1]

$$1 - e^{-x/\Lambda}. \tag{137}$$

(*b*) *Direct Experimental Measurements*: Formula (134) affords a direct experimental test of the demonstration and also a method of measuring the mean free path. This cannot be easily carried out, however, with a ray of ordinary molecules because the counting of individual molecules is not simple. The experiment, however, may be performed with electrically charged particles since, in this case, the charge transferred affords a ready means of determining the number of particles. Measurements of this kind were first made by Lenard using electrons.[2] He found that the number of particles in a ray of electrons passing through a gas changes according to the relation

$$N = N_0 e^{-\alpha x}. \tag{138}$$

According to (134), the coefficient of absorption, α, equals $1/\Lambda$, that is, it is equal to the sum of the absorbing areas contained in 1 cc., namely,

$$\left[cN_A \pi \left(\frac{d_1 + d_2}{2} \right)^2 \right] \tag{139}$$

if x is measured in centimeters. More recent experimenters have used slower electron rays than did Lenard and have used rare gases as the absorbing medium.[3] Under these conditions the phenomenon is especially simple since the electrons collide elastically with the gas molecules as has been assumed in the treatment of collisions between molecules. In the case of the quicker rays used by Lenard, more complicated phenomena take place. W. Wien [4] has, moreover, performed similar experiments with canal rays. In this case, however, all the collisions are not of the same kind since a fraction α_1 of the collisions may excite the emission of light, a fraction α_2 may ionize the molecule and so forth. Then the molecule must move $1/\alpha_1$ times as far, in order to be excited to luminescence, than if each collision acted in this particular manner. There is then a special mean free path for the emission of light $\Lambda_1 = \Lambda/\alpha_1$ and the number of molecules emitting in the interval dx is

$$\frac{dN}{N} = \frac{dx}{\Lambda_1}, \text{ etc.} \tag{140}$$

[1] A number of other problems may be treated as corollaries of this. For example, the probability that a molecule will collide for the first time on a given path within the interval between x and $x + dx$ is equal to the product of the probability that it will not collide between 0 and x into the probability that it will collide in dx, therefore equalling

$$e^{-x/\Lambda} \frac{dx}{\Lambda}.$$

[2] P. Lenard, *Ann. Physik*, **12**, 714 (1903), esp. p. 737. Electrons of a cathode ray behave like the molecules of a gas in that they move in straight lines without "aiming." They are readily detectable by their electric charge and energy.

[3] J. Franck and G. Hertz, *Verh. deut. phys. Ges.*, **15**, 373 (1913); C. Ramsauer, *Ann. Physik*, **64**, 513; **66**, 546 (1921).

[4] W. Wien, *Ann. Physik*, **39**, 519 (1912); **70**, 1 (1923).

In some cases two opposed processes can be caused by collisions. Thus, there are present in a canal ray N_1 neutral molecules, with mean free path equal to Λ_1, and N_2 ions whose mean free path equals Λ_2. When the neutral molecules of the ray collide with the molecules of the surrounding gas, ionization of the gas molecules takes place. On the other hand, these ions are neutralized by collisions with the neutral molecules. Such phenomena are represented by the following formula:

$$dN_1 = -dN_2 = -N_1 \frac{dx}{\Lambda_1} + N_2 \frac{dx}{\Lambda_2}. \tag{141}$$

The first term on the right designates the decrease in number of neutral molecules due to ionization and the second term represents the increase due to neutralization. At the stationary state $dN_1 = -dN_2 = 0$, and therefore the equilibrium concentrations are proportional to the free paths:

$$\frac{N_1^0}{N_2^0} = \frac{\Lambda_1}{\Lambda_2}. \tag{142}$$

Born [1] and Bielz [2] have carried out an experiment analogous to Lenard's using a ray of neutral molecules. They allowed a ray of evaporated silver atoms to enter air at a very low pressure and measured the decrease in the number of the silver atoms by measuring the amount precipitated on a glass plate in a definite time for different distances of the plate along the ray.

The results obtained by this method, however, are not particular accurate. The exact values of the mean free path are obtained indirectly from measurements of viscosity (p. 156).

(c) *A More Exact Discussion*: It has been assumed up to this point that the molecules with which those of the ray collide are practically stationary, only the molecules of the ray being in motion. This assumption is justifiable for the case of electrons and canal rays. Upon considering ordinary gas molecules, however, the velocities of each of the participants in the collisions are of the same order of magnitude. This means that $\sqrt{\overline{\tilde{w}^2}}$ is the mean *relative* velocity of the molecules of both classes. If a Maxwellian distribution prevails it is seen from equation (119) that

$$\sqrt{\overline{\tilde{w}^2}} = \sqrt{\overline{w^2} + \overline{w'^2}},$$

where $\overline{w'^2}$ is the mean square velocity of the molecules receiving the collision. If all the molecules are the same $\overline{w'^2} = \overline{w^2}$ and $\sqrt{\overline{\tilde{w}^2}} = \sqrt{\overline{2w^2}}$.

It is seen from this that $\tilde{w} > w$, i.e., the receiving molecules act as if they were, on the average, moving toward the colliding molecules. On account of this, the number of collisions is increased in the ratio

$$\sqrt{\frac{\overline{\tilde{w}^2}}{\overline{w^2}}} = \sqrt{1 + \frac{\overline{w'^2}}{\overline{w^2}}}. \tag{144}$$

[1] M. Born, *Physik. Z.*, **21**, 578 (1920).
[2] F. Bielz, *Z. Physik*, **32**, 81 (1925).

The deduction is not yet entirely rigorous because in a group of molecules whose velocities are distributed according to the Maxwell Law, there are some which have especially high velocities. The absolute velocities of these are less different from their velocities relative to an average molecule than in the case for slow molecules, because the other molecules are moving slowly in comparison to them. On account of this, the free path of a given molecule depends to a certain extent upon the velocity of that molecule and, in fact, increases with its velocity. Upon taking an appropriate average, there is obtained for the mean free path of a molecule of type I in a mixture of two different kinds of molecules,

$$\frac{1}{\Lambda} = \left\{ \pi\sqrt{2}N_1 d_1^2 + \pi N_2 \left(\frac{d_1 + d_2}{2} \right)^2 \sqrt{\frac{m_1 + m_2}{m_2}} \right\} \frac{1}{v}. \tag{145}$$

Here the first summand takes into account the collisions with other molecules of type I and the second summand collisions with molecules of type II. It is seen that the mean free path is inversely proportional to the density as must follow from the discussion of the foregoing paragraphs in which the number of collisions was shown to be proportional to the density.[1]

A comparison of the case of a molecule moving among others of its own kind ($d_1 = d_2$), with the case in which a dimensionless molecule ($d_1 = 0$) (electron) moves among ordinary molecules (d_2), shows that the mean free path in the latter case is four times as large as the mean free path in the former case, provided that the molecules of diameter d_2 act like rigid spheres to the point molecule.

The number of collisions made by a molecule of type I with molecules of type II while the former traverses a distance of 1 cm. is

$$\frac{N_2}{v} \pi \left(\frac{d_1 + d_2}{2} \right)^2 \sqrt{\frac{m_1 + m_2}{m_2}}. \tag{146}$$

From this relation there is obtained for the number of collisions per molecule of type I per second (with $\overline{w} = 2\sqrt{2kT/\pi m_1}$),

$$2\sqrt{2\pi} \frac{N_2}{v} \left(\frac{d_1 + d_2}{2} \right)^2 \sqrt{\frac{m_1 + m_2}{m_1 m_2} kT}. \tag{147}$$

Since there are altogether N_1/v molecules of this type per cc., and since they move independently of each other, each experiences on the average the same number of collisions in equal intervals of time. Therefore the total number

[1] On the other hand, the average distance between the molecules is inversely proportional to the cube root of the density $\frac{1}{\sqrt[3]{N/v}}$. This latter magnitude is proportional to a kind of geometric mean of the mean free path and the square of the molecular diamater

$$\frac{1}{\sqrt[3]{\frac{N}{v}}} \sim \sqrt[3]{\Lambda d^2}.$$

of collisions between molecules of type I and molecules of type II per second per cc. equals

$$2\sqrt{2\pi}\,\frac{N_1N_2}{v^2}\left(\frac{d_1+d_2}{2}\right)^2\sqrt{\frac{m_1+m_2}{m_1m_2}kT}. \tag{148}$$

This quantity is seen to be proportional to the product of the densities of the two kinds of molecules present. The number of collisions between molecules of the same kind is (cf. eqn. (91))

$$\frac{N^2}{v^2}\,d^2\sqrt{\frac{4\pi kT}{m}} = \frac{N^2}{2v^2}\,|\bar{w}|\,\pi d^2. \tag{149}$$

The factor 1/2 is introduced since otherwise each collision would be counted twice, each molecule being counted once as the colliding particle and again as the receiving particle, in the same process.

To illustrate the numerical magnitude of these quantities the value of Λ for hydrogen may be taken. From viscosity measurements this is found to be 1.18×10^{-5} cm. at 0° and normal density. The average distance between the molecules under these conditions is 0.33×10^{-6}. At a pressure of 0.9×10^{-2} mm. Hg. Λ equals 1 cm. The mean distance between the molecules equals 1 cm. at a pressure of 2.8×10^{-17} mm. The number of collisions experienced by a hydrogen molecule per second at one atmosphere and 0°, is about 1.4×10^{10}, the total number per second per cc. being 1.9×10^{29}. At a pressure of 9/1000 mm., there are still 2.6×10^{19} collisions per second per cc. The number of collisions increases with the square root of the temperature, since it is proportional to w.

Special Types of Collisions: The present section is devoted to the deduction of a number of equations which are useful in the study of the velocity of gaseous reactions.[1]

(*a*) *Collisions with the Walls*: The first equation to be developed will give the number of collisions with the wall of the containing vessel in which the component of velocity perpendicular to the wall (ξ) is greater than some specified value ξ_0. The number of such collisions per sq. cm. per second equals [2]

$$\left.\begin{aligned}\int_{\xi_0}^{\infty}\xi dN &= \frac{N_0}{v}\frac{\displaystyle\int_{\xi_0}^{\infty}\xi e^{-\frac{m\xi^2}{2kT}}d\xi}{\displaystyle\int_{-\infty}^{+\infty}e^{-\frac{m\xi^2}{2kT}}d\xi}\\ &= \frac{N_0}{v}\sqrt{\frac{2kT}{m}}\frac{\displaystyle\int_{\sqrt{m\xi_0^2/2kT}}^{\infty}xe^{-x^2}dx}{\displaystyle\int_{-\infty}^{+\infty}e^{-x^2}dx},\end{aligned}\right\} \tag{150}$$

[1] Chap. XIV.

[2] Cf. equation (90) and p. 81.

where x is defined by equation (82). Upon performing the indicated integrations, the desired quantity is found to be

$$\frac{N_0}{2v}\sqrt{\frac{2kT}{\pi m}}\,e^{-\frac{m\xi_0^2}{2kT}}. \tag{151}$$

By an entirely similar calculation the number of collisions with the wall per sq. cm. per second in which the *total* velocity of the molecule is greater than w_0, is found to be

$$\frac{N_0}{2v}\sqrt{\frac{2kT}{\pi m}}\left(1+\frac{mw_0^2}{2kT}\right)e^{-\frac{mw_0^2}{2kT}}. \tag{152}$$

(*b*) *Collisions between Two Molecules*: The next important type of collision is one between two molecules of different types in which the *relative* velocity of the molecules is greater than some definite value $\tilde{w}_0$. Equation (117) gives the number of pairs of molecules whose relative velocities lie between $\tilde{w}$ and $\tilde{w}+d\tilde{w}$. Upon introducing space polar coordinates this expression becomes

$$d_w(N_1N_2) = N_{01}N_{02}\left(\frac{3}{2\pi(\overline{w_1^2}+\overline{w_2^2})}\right)^{3/2} \times e^{-\frac{3}{2}\frac{\tilde{w}^2}{\overline{w_1^2}+\overline{w_2^2}}}w^2dw\int_0^{\pi}\sin\vartheta d\vartheta\int_0^{2\pi}d\varphi. \tag{153}$$

If the right hand side of this expression be multiplied by $\tilde{w}$ and by the collision area of the colliding molecules, $\pi(d_1+d_2/2)^2$, there is obtained the number of collisions per second per cc. in which the relative velocity is between $\tilde{w}$ and $\tilde{w}+d\tilde{w}$. Integration of this quantity from $\tilde{w}_0$ to ∞ gives the number of collisions in which the relative velocity is greater than $\tilde{w}_0$. This is[1]

$$2\sqrt{2\pi}\,\frac{N_{01}N_{02}}{v^2}\left(\frac{d_1+d_2}{2}\right)^2\sqrt{\frac{m_1+m_2}{m_1m_2}kT} \times\left(1+\frac{m_1m_2}{m_1+m_2}\frac{\tilde{w}_0^2}{2kT}\right)e^{-\frac{m_1m_2}{m_1+m_2}\frac{\tilde{w}_0^2}{2kT}}. \tag{154}$$

It can also be shown that the number of collisions in which the component of relative velocity along the line of centers is greater than $\tilde{\xi}_0$ is

$$2\sqrt{2\pi}\,\frac{N_{01}N_{02}}{v^2}\left(\frac{d_1+d_2}{2}\right)^2\cdot\sqrt{\frac{m_1+m_2}{m_1m_2}kT}\,e^{-\frac{m_1m_2}{m_1+m_2}\frac{\tilde{\xi}_0^2}{2kT}}. \tag{155}$$

Equations (151) and (152) represent the number of collisions of two special types with the wall. Similarly equations (154) and (155) refer to special types of collisions between molecules. The number of collisions of the special

[1] Cf. equation (148). Here again the result must be divided by 2 for collisions between dentical molecules to avoid counting the same collision twice. P. Langevin and G. Rey, *Le Radium*, **10**, 142 (1913).

type are definite fractions of the whole. The analogy between equations (151) and (155) and between equations (152) and (154) should be noted.

(*c*) *Triple Impacts*: In the theoretical treatment of reactions of higher order than the second it is necessary to know the number of multiple collisions taking place. The most important of such collisions is one in which three molecules collide nearly simultaneously; a so-called triple impact. Such a process may be defined in a number of ways but the equations resulting from the various definitions agree in the order of magnitude assigned to the number of such collisions. If it be supposed that when two molecules collide they remain in contact an infinitely short time, the probability that a third molecule shall hit the pair while in contact is naturally zero. It is therefore necessary to define a finite time during which two molecules can still be said to be in collision. A triple collision is then one in which the third molecule hits the other two while they are still "in collision." One possible definition of the time of collision is the interval in which the distance between the two molecules is less than the molecular diameter.[1] From this definition it follows that approximately

$$\mathbf{N}_{III} : \mathbf{N}_{II} = d : \Lambda,$$

where $\mathbf{N}_{III}$ and $\mathbf{N}_{II}$ are the numbers of triple and double collisions per second per cc. respectively, d the diameter of the molecule and Λ its mean free path. Substituting for $\mathbf{N}_{II}$ and Λ from equations (149) and (145) it is found that

$$\left.\begin{aligned} \mathbf{N}_{III} = \mathbf{N}_{II}\frac{d}{\Lambda} &= 2\frac{N^2}{v^2}d^2\sqrt{\frac{2\pi kT}{m}}\cdot\frac{d}{\left(\frac{v}{\pi\sqrt{2}Nd^2}\right)} \\ &= 2\sqrt{2}\pi\frac{N^3}{v^3}d^5\sqrt{\frac{\pi kT}{m}}. \end{aligned}\right\} \qquad (156)$$

Similar equations can be developed for triple collisions between unlike molecules but these expressions can only be valid to within the order of magnitude due to the uncertainty of the definition of a triple collision.[2]

The Relation Between the Mean Free Path and the Temperature: The assumptions that have been made in the foregoing calculations lead to the conclusion that the mean free path is independent of the temperature. The indirect experimental determinations of the mean free path, however, show an increase with rising temperature. This means that the effective diameter of the molecules decreases with rising temperature.[3] Since the effective diameter of the molecules is found to vary with the temperature, they can no longer be regarded as rigid spheres, exerting no forces on each other except when in contact during collisions. Rather must the assumption now be made that

[1] K. F. Herzfeld, *Z. Physik*, **8**, 132 (1921).

[2] Cf. Syrkin, *Physik. Z.*, **24**, 236 (1923); R. C. Tolman, Statistical Mechanics with Applications to Physics and Chemistry. The Chemical Catalog Co., 1927, p. 247.

[3] If the molecules had a thermal expansion such as is observed in solid bodies, it would have the reverse effect.

molecules influence each other when they are comparatively far apart, but with forces which, in the light of all the experimental evidence, decrease rapidly with increasing distance. Let it be assumed, as a first approximation, that the forces are radial with spherical symmetry; that is, the force between two molecules regardless of their orientation is given by the relation A/r^n, where r is the distance between the centers. It is found from experimental data that n must be assumed to have rather large values (5–12).

Under these circumstances the previous definition of the mean free path as that distance which a molecule can traverse without being affected by others, loses its meaning because molecules now affect each other at relatively great distances (with decreasing strength) so that a collision is no longer sharply defined. Nevertheless, it is possible to frame other more suitable definitions. One presentation, which is especially useful, is due to Sutherland,[1] who considers the molecules as hard spheres which exert attractive forces on one another. In this case, as before, a collision may be defined as a process in which the surface of two molecules touch, or in which the distance between the centers is d. The forces between the molecules do not change the immediate effect of the collisions, which take place exactly as in the former case of rigid, force-free spheres. The forces, however, affect the motion before and after the collision. Consider two molecules moving in such a manner that they are not aimed toward each other. They would not collide if it were not for the attractive forces. These latter, however, draw the molecules together so that a collision takes place. The effect of the forces is therefore to increase the number of collisions and thereby decrease the mean free path. The greater the molecular velocities (the greater the temperature) the smaller is this deflection, provided that the forces remain constant. Therefore, the increase in number of collisions is less at high temperatures and the mean free path is increased. At very high temperatures the molecules move as if there were no attractions between them because their kinetic energy is so large in comparison to the potential energy of the attractive forces that their mean free path is given by (130). The quantitative relation is [2]

[1] W. Sutherland, *Phil. Mag.*, (V) **36**, 507 (1893).

[2] Consider a stationary molecule toward which another one is moving in such a manner that, disregarding for the moment the attractive forces, the nearest approach of the centers of the two molecules is r_0. The attractive force is a function of the distance alone and may be derived from a potential energy by the equation

$$F = -\frac{\partial \epsilon_p}{\partial r} \tag{157}$$

This potential energy ϵ_p will be set equal to zero at $r = \infty$. Assume a system of polar coordinates with the stationary molecule as origin. At the beginning of the process, when the two molecules are at an infinite distance, the velocity of the moving molecule is equal to the original relative velocity $\bar{w}_0$ of the two particles:

$$\overline{\bar{w}^{02}} = \frac{3kT}{m_1 m_2}(m_1 + m_2). \tag{158}$$

$$\Lambda = \frac{\Lambda_\infty}{1 + \frac{C}{T}} = \Lambda_\infty \frac{T}{C + T}. \tag{165}$$

The values of C calculated from the experimental data vary from 50 to 300, and increase with increasing attractive forces (p. 157). They are proportional to the work obtained when two molecules are brought close together. The factor of proportionality, however, still depends upon the special form of the law of force between the molecules.[1] Since the Sutherland constant C is related to the forces between the molecules and to their diamaters, it is also closely connected with the van der Waals constants a and b, the latent heat of evaporation, etc. In general these quantities are large for high boiling liquids

The velocity $\tilde{w}$ can be resolved into two components, one in the direction of the radius vector and another perpendicular to it:

$$\tilde{w}^2 = \left(\frac{dr}{dt}\right)^2 + r^2\left(\frac{d\varphi}{dt}\right)^2. \tag{159}$$

and is initially $\tilde{w}_0$ as has been mentioned before. The law of conservation of energy then states that

$$\left(\frac{dr}{dt}\right)^2 + r^2\left(\frac{d\varphi}{dt}\right)^2 - \tilde{w}_0^2 = -\frac{\epsilon_p}{m}, \tag{160}$$

where $-\epsilon_p$ is the positive work of the attractive force. The second summand is determined from the law of areas, $r^2 \dfrac{d\varphi}{dt}$ = constant, the left hand side of which equation, the moment of area divided by the mass, is initially $\tilde{w}_0 r_0$. The former equation then becomes

$$\left(\frac{dr}{dt}\right)^2 + \frac{1}{r^2} r_0^2 \tilde{w}_0^2 - \tilde{w}_0^2 = -\frac{\epsilon_p}{m}. \tag{161}$$

The point of closest approach, $r_{\min}$, is defined by the usual conditions for a minimum

$$\left(\frac{dr}{dt}\right)_{\min} = 0$$

and therefore

$$\frac{r_0^2}{r_{\min}^2} = 1 - \frac{\epsilon_p}{m\tilde{w}_0^2}. \tag{161'}$$

A collision will occur for all values of r_0 for which $r_{\min} \leqq d$, i.e. when

$$r_0^2 \leqq d^2\left(1 - \frac{\epsilon_p}{m\tilde{w}_0^2}\right). \tag{162}$$

Upon suitable averaging over $1/\tilde{w}_0^2$, whereby it is to be noted that $\tilde{w}_0^2$ is, on the average proportional to T (158), the condition of collision becomes

$$r_0^2 \leqq d^2\left(1 + \frac{C}{T}\right), \tag{163}$$

instead of

$$r_0^2 \leqq d^2, \tag{164}$$

the factor signifying a *greater effective molecular diameter* at low temperatures.

[1] S. Chapman, *Phil. Trans.*, (A) **216**, 279 (1916); D. Enskog, *Physik. Z.*, **12**, 56, 533 (1911).

and vice versa. Keyes [1] has shown that C is directly proportional to the Lorenz-Lorentz molecular polarization.

Maxwell [2] has found that especially simple relations are obtained if the force varies with the inverse fifth power of the distances because [3] in that case the decrease of the effective cross-section with increasing velocity is exactly compensated by the increase in the number of collisions caused by the increasing relative velocity. Many calculations which, for other laws of force, can only be obtained by approximation, can in this case be carried to completion. With this law of force the mean free path is proportional to the square root of the temperature.

Reinganum [4] attempted to derive the relation between the mean free path and the temperature from the assumption that the molecules form clusters. The Boltzmann Law states that, everything else being the same, the density at a place of lower potential energy, that is, a place toward which the attractive forces act, or where a molecule does work on entering, is greater by the factor $e^{-\frac{\epsilon_p}{kT}}$. The potential energy in the immediate neighborhood of a molecule is smaller as a result of the attractive forces and the density of the other molecules is therefore greater, there being formed so-called clusters or clumps. If the temperature is raised this will take place to a less extent, since, as has been pointed out previously, such differences in density are decreased by rising temperature due to the exponential term approaching unity.

According to Reinganum, the formula,

$$\sqrt{2}\pi \frac{N_A}{V} d^2 = \sqrt{2}\pi N_A c d^2, \tag{166}$$

which gives the number of collisions experienced by a given molecule for 1 cm, must be modified by replacing the average density of the molecules, $N_A c_0$, with the density of the molecules in the cluster in the immediate neighborhood of the given molecules. Upon substituting for c,

$$c_0 e^{-\frac{\epsilon_p}{kT}} = c_0 e^{\frac{C'}{T}}, \tag{167}$$

there is obtained,

$$\Lambda = \Lambda_\infty e^{-\frac{C'}{T}}. \tag{168}$$

Upon expanding this relation into a series of terms in C'/T it is seen to be identical with equation (165) if the squared and higher terms are neglected. Even for large temperature intervals the difference between the values given by the two relations is not considerable.[5]

[1] F. G. Keyes, *Z. physik. Chem.*, **130**, 709 (1927).

[2] C. Maxwell, *Phil. Mag.*, (IV) **32**, 390 (1866); **35**, 129, 185 (1868). Cf. also L. Boltzmann, Vorlesungen uber Gastheorie I, 153.

[3] L. Boltzmann, *Wien. Ber.*, **81**, 117 (1880).

[4] M. Reinganum, *Physik. Z.*, **2**, 241 (1901).

[5] K. Rappenecker, *Z. physik. Chem.*, **72**, 719 (1910).

There will now be given a rigorous proof of Maxwell's Distribution Law [1] and an outline of the exact methods used to attack the problems of gases not at equilibrium.

The Boltzmann Equation: The gas under consideration will be assumed to be composed of spherical molecules. At any instant throughout the gas some distribution of the density of the molecules and their velocities will prevail. The spatial distribution of the molecules may be represented in the usual three-dimensional space described by the rectangular coordinates x, y, z, in which there is a state point for each molecule. Similarly, the distribution of the molecular velocities may be represented in the " velocity space " described by the rectangular coordinates ξ, η, ζ (p. 78). The general distribution function f, which is to be evaluated, will therefore give the densities of the state points in these two systems of coordinates in terms of the coordinates.

It must be emphasized that the prevailing distribution is altered or maintained by the *irregularity* of the molecular collisions. Suppose, for example, that, at a given instant, some particular molecule is stationary. This molecule would remain motionless indefinitely if it experienced only balanced collisions, that is to say, if the effect of each molecule hitting the stationary one were exactly compensated by the impact of another molecule hitting the stationary one at the same time at a point diametrically opposite the point of collision of the first and with a velocity equal and opposite to that of the first. Such a regular sequence, however, can only occur infrequently; the stationary molecule is set in motion as a result of the irregularity of the collisions.

Consider now a gas in which the velocity and space distributions are arbitrary. In general the gas will not be at equilibrium. It will be necessary to investigate in detail how this arbitrary distribution will change in the course of time as a result of collisions between molecules, motions of the molecules and external forces. The gas is said to be at equilibrium if any particular distribution obtains which does not change with the time.

In order to find the formula for the space and velocity distributions of the molecules it will be convenient to select a particular group of molecules and investigate the change in the number of molecules in this group. The conditions which must be fulfilled by a molecule in order that it be a member of this selected group will be first, its spatial coordinates must be in the intervals x to $x + \Delta x$, y to $y + \Delta y$ and z to $z + \Delta z$, and second, its components of velocity must be within the limits ξ and $\xi + \Delta\xi$, η and $\eta + \Delta\eta$, ζ and $\zeta + \Delta\zeta$. In other words, the molecule's statepoint in the x, y, z space must be within the element of volume ΔV at x, y, z and in the velocity space must be within an element of volume $\Delta\omega = \Delta\xi\Delta\eta\Delta\zeta$ at the point ξ, η, ζ. A molecule fulfilling these two conditions will be said to belong to group A.

[1] Clerk Maxwell, *Phil. Mag.*, (IV) **35**, 185 (1868); *Phil. Trans.*, **170**, 231 (1880); L. Boltzmann, *Wien. Ber.*, **58**, 517 (1868); **66**, 275 (1872); **96**, 891 (1887); H. A. Lorentz, *ibid.*, **95**, 115 (1887). On page 93 ff. we assumed the thermodynamical result of equal kinetic energy throughout. No such assumption will be made now. Accordingly this result will be a kinetic proof of the assumption.

The number of molecules in Group A will be proportional to ΔV and $\Delta\omega$ provided these are chosen neither too large nor too small (cf. p. 79). It will furthermore be proportional to the distribution function f, which, in the general case, will be a function of x, y, z and ξ, η, ζ. Therefore

$$\Delta N = Nf(x, y, z, \xi, \eta, \zeta)\Delta V\Delta\omega, \tag{169}$$

where ΔN is the number of molecules in Group A, N the total number of molecules present and f the distribution function to be evaluated.

Now N can change in the course of time by means of three different processes. In the first place, each time a molecule of Group A experiences a collision its velocity is changed by a finite amount and it is therefore removed from the group. It will therefore be necessary to calculate accurately the number of collisions experienced by the molecules of Group A. To do this a new class of molecules (Group B) will be taken under consideration. To belong to this group a molecule's statepoints must lie within the elements ΔV_1, and $\Delta\omega_1$, situated at the points x_1, y_1, z_1, and ξ_1, η_1. ζ_1. The number of molecules in Group B will be

$$\Delta N_1 = Nf(x_1, y_1, z_1, \xi_1, \eta_1, \zeta_1)\Delta V_1\Delta\omega_1. \tag{170}$$

For abbreviation the arguments of the distribution function will be omitted, the appropriate subscripts being appended to the symbol f. Thus equation (170) will be written

$$\Delta N_1 = Nf_1\Delta V_1\Delta\omega_1. \tag{171}$$

By a method of reasoning entirely similar to that developed on p. 118, it is found that the number of collisions per second between a single molecule of Group A and all the molecules of Group B is

$$d^2\frac{\Delta N_1}{\Delta V}Z, \tag{172}$$

where d is the molecular diameter and Z a quantity depending on the nature of the molecule and the type of collision. If the molecules are perfectly elastic,

$$Z = \int_0^{\pi/2} |\tilde{w}| \cos\vartheta \sin\vartheta d\vartheta \int_0^{2\pi} d\varphi, \tag{173}$$

where $|\tilde{w}|$ is the magnitude of the relative velocity, ϑ the angle between the direction of the relative velocity and the line of centers at the instant of collision, and φ an angle determining the orientation of the plane containing the line of centers and the direction of the relative velocity. Substituting from equation (171), equation (172) becomes

$$Nd^2f_1\Delta\omega_1 Z. \tag{174}$$

In order to determine the total number of collisions experienced by a molecule of Group A, ξ_1, η_1, ζ_1 must be integrated over all values. Multiplying by the number of molecules in Group A (ΔN, equation (169)) the total number of

collisions experienced by the molecules of Group A is found to be

$$Nf\Delta V\Delta\omega Nd^2\int_{\omega_1} Zf_1 d\omega_1 = N^2d^2\Delta V\Delta\omega\int_{\omega_1} Zff_1 d\omega_1. \tag{175}$$

This is therefore the number of molecules leaving Group A per unit time as a result of collisions. On the other hand, some molecules formerly not belonging to Group A will be thrown into it by collisions. It will now be necessary to calculate the number of these molecules entering Group A as a result of their collisions.

The velocity of a molecule of Group A after collision will be denoted by ξ^*, η^*, ζ^*, and that of a molecule of Group B after collision by $\xi_1{}^*$, $\eta_1{}^*$, $\zeta_1{}^*$ (Groups A* and B*). $\xi^* \ldots \zeta_1{}^*$ will depend on $\xi \ldots \zeta_1$, on ϑ and φ and on the nature of the molecules.

Now the process of molecular collision is mechanically reversible, that is, if a collision between a molecule of Group A and one of Group B changes them to Groups A* and B* respectively, then a collision between molecules of Groups A* and B* will result in molecules of Groups A and B provided ϑ

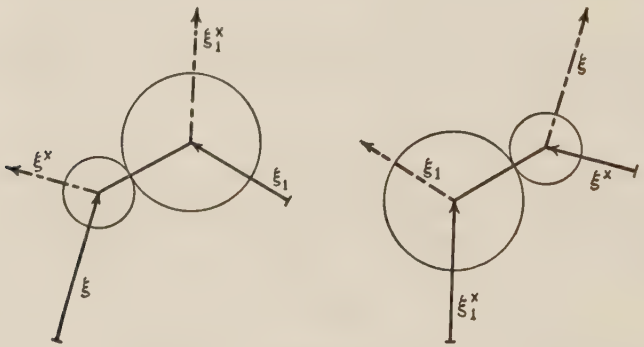

Fig. 22.

and φ are the same for the two collisions. (See Fig. 22.) The number of molecules of Group A entering into collision in unit time, and hence leaving Group A is given by equation (175). By reasoning entirely similar to that used in the deduction of this latter equation it can be shown that the number of molecules of Group A* emerging from collision per unit time and hence entering Group A is

$$N^2d^2\Delta V^*\Delta\omega^*\int_{\omega_1{}^*} Z^*f^*f_1{}^*d\omega_1{}^*. \tag{176}$$

It can be shown that $\Delta V^* = \Delta V$; $\Delta\omega^* = \Delta\omega$ and $\Delta\omega_1{}^* = \Delta\omega_1$; $Z = Z^*$. Therefore the net decrease in the number of molecules in Group A as a result of collisions is

$$N^2d^2\Delta V\Delta\omega\int Z(ff_1 - f^*f_1{}^*)d\omega_1. \tag{177}$$

The second way in which the number of molecules of Group A can change is by motion of the molecules in and out of the *volume* element. The number of molecules crossing the boundary perpendicular to the X-axis at the point x from left to right will be (Fig. 23, and p. 82)

$$\xi\left(\frac{\Delta N}{\Delta V}\right)_x \Delta y\Delta z = N\xi f_x \Delta\omega\Delta y\Delta z. \tag{178}$$

This is the number of molecules entering Group A per second through this

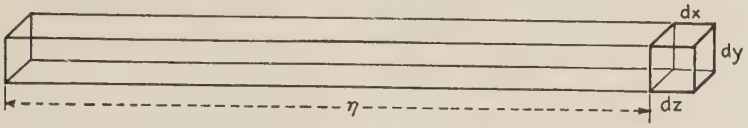

FIG. 23.

face of the cubical element of volume. The flow of molecules from left to right through the opposite face of the element equals

$$\xi\left(\frac{\Delta N}{\Delta V}\right)_{x+\Delta x} \Delta y\Delta z = N\xi f_{x+\Delta x}\Delta\omega\Delta y\Delta z. \tag{179}$$

If the density is not everywhere the same f_x is not equal to f_{x+dx} but

$$f_{x+\Delta x} = f_x + \frac{\partial f}{\partial x}\Delta x. \tag{180}$$

Therefore, the net loss to Group A by flow through these two boundaries of the cube is

$$N\xi\left(f_x + \frac{\partial f}{\partial x}\Delta x - f_x\right)\Delta\omega\Delta y\Delta z = N\xi\frac{\partial f}{\partial x}\Delta\omega\Delta V. \tag{181}$$

Taking account of the flow through the other two pairs of faces of the cube, the total net loss to Group A resulting from motion of the molecules between collisions is found to be

$$N\left(\xi\frac{\partial f}{\partial x} + \eta\frac{\partial f}{\partial y} + \zeta\frac{\partial f}{\partial z}\right)\Delta\omega\Delta V. \tag{182}$$

The third way in which the number of molecules in Group A can be changed is by the action of external forces which change the molecular velocities during the intervals between collisions and therefore cause the statepoints in the velocity space to move in or out of $\Delta\omega$ in a continuous manner. (At collisions they jump to another place.) Consider a field of force, the intensity of which at any point may be represented by the components of force F_x, F_y, F_z acting at that point. Then the equations representing the motion of the molecules

between collisions are

$$m\frac{d\xi}{dt} = F_x; \qquad m\frac{d\eta}{dt} = F_y; \qquad m\frac{d\zeta}{dt} = F_z, \tag{183}$$

where m is the mass of the molecule and t the time. The present calculation is exactly similar to the preceeding except that instead of calculating the flux of molecules moving with the velocity ξ, η, ζ through the boundaries of the element ΔV the problem now requires the calculation of the flux of state-points in the velocity-space moving with the velocity $d\xi/dt$, $d\eta/dt$, $d\zeta/dt$ through the boundaries of the element $\Delta\omega$. The net loss to Group A as a result of the external forces is therefore

$$N\left(\frac{d\xi}{dt}\frac{\partial f}{\partial \xi} + \frac{d\eta}{dt}\frac{\partial f}{\partial \eta} + \frac{d\zeta}{dt}\frac{\partial f}{\partial \zeta}\right)\Delta\omega\Delta V, \tag{184}$$

which, by equations (183), equals

$$N\left(\frac{F_x}{m}\frac{\partial f}{\partial \xi} + \frac{F_y}{m}\frac{\partial f}{\partial \eta} + \frac{F_z}{m}\frac{\partial f}{\partial \zeta}\right)\Delta\omega\Delta V. \tag{185}$$

Equations (177), (182) and (185) give the decreases in the number of molecules in Group A due to collisions, motion of the molecules and external forces. The sum of these three quantities must equal the total decrease in the number of molecules in Group A which is

$$-N\frac{\partial f}{\partial t}\Delta\omega\Delta V.$$

Therefore, after dividing through by $N\Delta\omega\Delta V$, there is obtained the fundamental equation of the theory of gases:[1]

$$\frac{\partial f}{\partial t} + \frac{F_x}{m}\frac{\partial f}{\partial \xi} + \frac{F_y}{m}\frac{\partial f}{\partial \eta} + \frac{F_z}{m}\frac{\partial f}{\partial \zeta} + \xi\frac{\partial f}{\partial x} + \eta\frac{\partial f}{\partial y} + \zeta\frac{\partial f}{\partial z} = -Nd^2\int_{\omega_1} Z(ff_1 - f^*f_1^*)d\omega. \tag{186}$$

In the case of a mixture of two gases there must be added another term to take account of the collisions between molecules of the two different gases. This term is

$$-d_{12}^2N'\int(ff_1' - f^*f_1'^*)d\xi'd\eta'd\zeta'\int|\tilde{w}_{12}|\cos\vartheta\sin\vartheta d\vartheta d\varphi, \tag{187}$$

where the primed symbols denote the corresponding quantities for the second component of the mixture. An entirely analogous expression holds for the other constituent itself.

[1] L. Boltzmann, *Wien. Ber.*, **66**, 213 (1872); **72**, 427 (1875). For a treatment involving the Theory of Relativity, see F. Jüttner, *Ann. Physik*, **34**, 856 (1911); E. Kretschmann, *Physik. Z.*, **21**, 484 (1920); **25**, 162 (1924).

Furthermore, if it is assumed that the molecules no longer are elastic spheres, but act upon each other according to some law of force, the only change in the fundamental equation is to replace the constant cross section πd^2 of the molecules with one dependent on the velocity and to change the formal relation between the velocities before and after collision.

Gases in Equilibrium: In the simplest case of equilibrium in which there are no external forces and where the density is constant throughout the space under discussion, the left hand side of (186) must be zero since, in this particular case, f is not a function of x, y, z. The condition that the integral on the right shall vanish is that at every point of the space

$$ff_1 = f^*f_1^*. \tag{188}$$

Since, furthermore, in this case there is no favored direction of velocity, f can only depend on the magnitude of the velocity $w = \sqrt{\xi^2 + \eta^2 + \zeta^2}$ and not upon the individual components ξ, η, ζ. Therefore

$$f(w) \cdot f(w_1) = f(w^*) \cdot f(w_1^*). \tag{189}$$

Now w and w_1 are entirely arbitrary and w^* may be arbitrarily varied to a certain extent by changing the angle $\vartheta \cdot w_1^*$ is then determined by the law of conservation of energy,

$$w_1^{*2} = w^2 + w_1^2 - w^{*2}. \tag{190}$$

With this value of w_1^* equation (189) can only be satisfied for arbitrary values of w, w_1 and w^* if [1]

$$f = Ae^{-\beta m w^2}, \tag{196}$$

which is Maxwell's Distribution Law for the state of equilibrium. For a mixture of several gases, the analogous formula is

$$f(w)f'(w_1') = f(w^*)f'(w_1'^*) \quad \text{and} \quad m'w_1^{*'2} = mw^2 + m'w_1'^2 - mw^{*2}, \tag{197}$$

whence

$$f' = A'e^{-\beta m' w'^2}.$$

The magnitude β is therefore identical for all the components of the gaseous

[1] Define a function

$$\varphi(w^2) = lnf(w). \tag{191}$$

Then

$$\varphi(w^2) + \varphi(w_1^2) = \varphi(w^{*2}) + \varphi(w^2 + w_1^2 - w^{*2}). \tag{192}$$

Upon differentiating this with respect to w, keeping the other independent variables w_1 and w^* constant, this becomes

$$2w\dot{\varphi}(w^2) = 2w\dot{\varphi}(w^2 + w_1^2 - w^{*2}), \tag{193}$$

where $\dot{\varphi}(x) = d\varphi/dx$. Since the left hand side of this does not contain w_1 and w^*, the right hand side must also be independent of these quantities. Therefore

$$\dot{\varphi}(w^2) = -B \tag{194}$$

and

$$\varphi(w^2) = -Bw^2 + \text{const.} \tag{195}$$

mixture. Further, $1/\beta$ is seen to be 4/3 times the mean kinetic energy, and the latter is therefore the same for all the components of the mixture. Considerations such as those of pp. 83 ff. show the equality of this quantity for any two gases placed in thermal contact and therefore its significance as a measure of the temperature.

If the gas is situated in a field of force such that

$$F_x = -\frac{\partial \epsilon}{\partial x}; \qquad F_y = -\frac{\partial \epsilon}{\partial y} \qquad F_z = -\frac{\partial \epsilon}{\partial z},$$

the Maxwell-Boltzmann Law follows at once from equation (186).

Gases Not at Equilibrium: If equilibrium does not prevail, the entire equation (186) must be solved, in which case it can in general be assumed that the deviations from the equilibrium distribution are not large. The solution is written in the form of a power series in which the first term is the Maxwell distribution and the following terms are multiplied by increasing powers of a small parameter Λ:

$$f = f^{(0)} + \Lambda f^{(1)} + \Lambda^2 f^{(2)}, \tag{198}$$

where $f^{(0)}$ denotes the Maxwell distribution. The method of successive approximation is then used, which requires that the equation be satisfied for each power of Λ. Thus, for example, $f^{(1)}$ is inserted in the left hand side of the equation whereupon the right hand side becomes

$$-d^2 N_0 Z \int [f^{(0)} f_1^{(1)} + f^{(1)} f_1^{(0)} - f^{*(0)} f^{*(1)} - f^{*(1)} f_1^{*(0)}] d\omega_1. \tag{199}$$

This gives an equation which is linear in the unknown $f^{(1)}$.

This method was introduced by Boltzmann,[1] used to a large extent by H. A. Lorentz,[2] and brought to a systematic mathematical form by Hilbert.[3]

The calculations have been carried out for internal friction, heat conduction, diffusion, etc., for the following cases by Enskog: elastic spheres, spheres repelling each other with forces of the form K/r^n, where n is arbitrary and for elastic spheres with attractive forces.[4] Maxwell [5] has used another method for the accurate calculation of the phenomena treated approximately in the next section.

If equation (186) be integrated over all velocities there is obtained an expression for the change in the total number of molecules contained in the volume element. The result is the so-called equation of continuity of hydrodynamics which expresses the indestructibility of matter.

Just as in equation (186) the change in the number of molecules occurring in a given region of the velocity space, due to different causes, has been cal-

[1] L. Boltzmann, *l.c.*, also Ges. Abh. II, p. 388 ff.; III, p. 3; Gastheorie, I, p. 184.

[2] H. A. Lorentz, *Arch. neerl.*, **16**, 1, 1881.

[3] D. Hilbert, Vorlesungen über Integralgleichungen, Leipzig 1912.

[4] D. Enskog, Diss. Upsala 1917; *Physik. Z.*, **12**, 56, 533 (1911); *Ark. för Mat. Astr. och Fysik*, **16**, No. 16 (1921).

[5] Clerk Maxwell, *Phil. Trans.*, **157**, 49, (1867); *Phil. Mag.*, (IV) **35**, 129, 185 (1868).

culated, so may the change in any other magnitude carried by the molecules be calculated. Examples of such magnitudes are the kinetic energy and the momentum. Furthermore, it is possible to set up an equation expressing the change in that part of the given quantity which is due to the molecules of Group A. Upon integrating over all velocities there is obtained the change in the magnitude under consideration in the given element of volume due to external forces, transportation through the sides of the volume element by molecules and collisions. Thus if the indicated calculations are carried through for the three components of momentum there are obtained the hydrodynamic equations of motion in the general form, that is, in which the pressure forces depend upon the direction.

Similarly, if the kinetic energy is used instead of the momentum the equation of heat conduction is obtained.

In order to calculate the relation between the external forces and the state of the gas, an expression analogous to Hook's Law for solid bodies, the distribution function f must be used. If Maxwell's distribution $f^{(0)}$ is used for this quantity as a first approximation, there is obtained the relation for a non-viscous liquid without heat conduction (that is, at uniform temperature) and with the equation of state $pV = RT$. Upon introducing further terms of the series development of f (in which Λ can be shown to be a quantity of the character and order of magnitude of the mean free path) there is obtained a more complete equation containing the stress tensor.

Maxwell was the first to carry through this type of calculation. Later Lorentz applied it to the propagation of sound in gases, which phenomenon may be said to be explained kinetically in this fashion in so far as it follows from the hydrodynamic equations of motion. Both the form of these equations and the constants contained in them may be calculated from the kinetic theory of gases, i.e., brought back to molecular constants. On the other hand the process has never been treated directly from the kinetic theory since such a treatment would be extremely complicated. To be able to perform the calculations, Maxwell had to assume that the molecules repel each other with a force inversely proportional to the fifth power of the distance. In this case it is noteworthy that it is unnecessary to evaluate f explicitly to obtain the equations of viscosity, heat conduction and diffusion. Chapman[1] has developed a rigorous method for the treatment of these problems along similar lines, assuming a generalized law of interaction between the molecules. From an analysis of the equations of transfer of the quantities ξw^{2n} and $\xi^2 w^{2n}$ he shows that the deviation from the Maxwellian distribution may be expressed as the sum of four functions. He then expresses these functions as power series in w^2 and, after evaluating the constants in these series by equations of the type (198) and (199) he determines the coefficients of viscosity, heat conduction and diffusion for the laws of force previously calculated by Enskog. Chapman's analysis is extended to take account of mixtures of two gases.

[1] S. Chapman, *Phil. Trans.*, **211**, 433 (1912); **216**, 279 (1916); **217**, 115 (1917); *Proc. Roy. Soc.*, **93A**, 1 (1912).

H-Theorem: The considerations which permit the calculation by means of equation (162) of the change of some quantity in the element of volume due to collisions between the molecules, led Boltzmann [1] to a conclusion, which is of great importance to the theory of gases, in the course of an investigation of the change in the quantity lnf summed over all the molecules. He defined a function by the equation

$$\mathrm{H} = N_0 \int lnf \cdot f d\xi d\eta d\zeta dV. \tag{200}$$

H is calculated by introducing the coordinates and velocities of each molecule into lnf and summing over all the molecules in the volume, that is, integrating over $N_0 f d\xi d\eta d\zeta dV$. If equation (186) is multiplied through with $lnf N_0 d\xi d\eta d\zeta dV$ and integrated there is obtained upon the left $d\mathrm{H}/dt$, the total change in the quantity H in the volume under consideration: [2]

$$\frac{d\mathrm{H}}{dt} = -d^2 N_0^2 \int\int lnf(ff_1 - f^*f_1^*) d\xi d\eta d\zeta d\xi_1 d\eta_1 d\zeta_1 dVZ. \tag{202}$$

Since the integral of lnf over *all* the molecules is the same regardless of the particular group which is used as a starting point, lnf may be replaced in equation (202) by $(lnf + lnf_1)/2$. The expression, however, is not yet sufficiently symmetrical.

Let us introduce besides the " direct collisions," the reverse collisions formerly designated by a star. There is then obtained the same value by writing

$$\frac{d\mathrm{H}}{dt} = -d^2 N_0^2 \int\int \frac{lnf^* + lnf_1^*}{2} (f^*f_1^* - ff_1) dV^* d\omega^* d\omega_1^* Z. \tag{203}$$

Adding this to the former expression and dividing by 2 gives

$$\frac{d\mathrm{H}}{dt} = -\frac{d^2 N_0^2}{4} \int\int (lnff_1 - lnf^*f_1^*)(ff_1 - f^*f_1^*) d\xi d\eta d\zeta d\xi_1 d\eta_1 d\zeta_1 dVZ. \tag{204}$$

The right hand side of this expression has always the same sign, since, whenever one of the parentheses changes sign, the other changes sign simultaneously. H is therefore a quantity which decreases in all possible changes, and is therefore analagous to negative entropy.

As a matter of fact a direct calculation shows that $\mathrm{H} = -(S/k) + \text{const.}$ Thus, a mechanical explanation is given of the experimental result that the entropy of a system always increases (Boltzmann's H-Theorem) (cf. Chap. II).

The Specific Heat of a Diatomic Gas: The greater part of the foregoing discussion has been concerned only with monatomic gases. Such a gas has

[1] L. Boltzmann, *Wien. Ber.*, **66**, 275, (1872); Gastheorie, I, p. 32, 124.

[2] More exactly

$$\frac{d\mathrm{H}}{dt} = N_0 \int \left(lnf \cdot \frac{df}{dt} + \frac{1}{f} \cdot f \frac{df}{dt} \right) d\xi d\eta d\zeta dV, \tag{201}$$

The last summand of this expression, however, vanishes upon integration, if the total number of molecules is constant.

only three degrees of freedom per molecule. Because of this fact the average kinetic energy of the molecule was found to be $\frac{3}{2}kT$. Since this is the only type of energy present in the gas, $U = \frac{3}{2}RT$. Correspondingly, the calculated value for the molecular heat capacity is $C_v = 3R/2$. As will be seen from the following table, this prediction is confirmed by experiment.

TABLE II

	T° Abs.	C_v	
He.....	291	3.008	Perfect gas interval,[1]
	93	2.949	
	26	2.99	
	22	3.00	9.3 mols litre [2]
	18	3.02	
A.....	288	3.07	Perfect gas interval [3]
	93	2.86	
Hg.....	∞550	2.97	Calculated from $C_p/C_v = 1.666$ [4]

[1] K. Scheel and W. Heuse, *Ann. Physik*, **40**, 473 (1913).
[2] A. Eucken, *Verh. deut. phys. Ges.*, **18**, 4 (1916).
[3] W. Heuse, *Ann. Physik*, **59**, 86 (1919).
[4] A. Kundt and E. Warburg, *Pogg. Ann.*, **157**, 353 (1876).

On the other hand, di- and polyatomic gases have higher specific heats.

Consider first a diatomic gas, the molecule of which of mass m contains two atoms of masses m_1 and m_2, the distance between the two atoms being d. The center of gravity of the molecule is on the line joining the centers of the atoms and divides this line in such a manner that the distance from the center of gravity to atom I is

$$d_1 = d\frac{m_2}{m_1 + m_2}; \tag{205}$$

and the distance from the center of gravity to atom II is

$$d_2 = d\frac{m_1}{m_2 + m_1}. \tag{206}$$

The molecule can now rotate about its center of gravity. In order to fix the orientation of the molecule imagine a straight line fixed in space which is to serve as the polar axis of a system of space polar coordinates having its origin at the center of gravity of the molecule in question. The position of the axis of the molecule is then determined by the geographical latitude, $\frac{\pi}{2} - \vartheta$, and

the geographical longitude, φ, of, for example, atom I. Atom I can therefore rotate on a sphere of radius d_1, element of surface $d_1^2 \sin \vartheta d\vartheta d\varphi$ and total area $4\pi d_1^2$. The rotational kinetic energy of atom I can be resolved into two parts corresponding to the two components of velocity, one of which is along a parallel of latitude and the other is along a meridian of longitude. The first component of velocity is $d_1 \sin \vartheta \dot{\varphi}$, $d_1 \sin \vartheta$ being the radius of the particular parallel of latitude. The second component of velocity is $d_1\dot{\vartheta}$. The rotational kinetic energy of atom I is therefore

$$\frac{m}{2} d_1^2(\dot{\vartheta}^2 + \sin^2 \vartheta \dot{\varphi}^2), \tag{207}$$

where the superposed dots signify derivatives with respect to the time (e. g. $\dot{\varphi} = d\varphi/dt$). A similar equation holds for atom II so that the total rotational kinetic energy of the molecule is

$$\epsilon_r = \left(\frac{m_1}{2} d_1^2 + \frac{m_2}{2} d_2^2 \right) (\dot{\vartheta}^2 + \sin^2 \vartheta \dot{\varphi}^2). \tag{208}$$

The quantity $m_1 d_1^2 + m_2 d_2^2$ equals the moment of inerita I of the molecule and, by elimination of d_1 and d_2, can be brought to the form

$$I = \frac{m_1 m_2}{m_1 + m_2} d^2. \tag{209}$$

To obtain the law of distribution for the rotational degrees of freedom it is necessary to distinguish between the distribution of orientations, corresponding to the spatial distribution of the molecules in the former treatment, and the distribution of the velocities of rotation, corresponding to the velocities of translation in the former treatment.

Orientations which appear equally often are those in which the axis of the molecule sweeps out equally large cones, or those in which atom I describes equally large areas on the sphere of radius d_1. The probability of an orientation in which the colatitude is between ϑ and $\vartheta + d\vartheta$ and the longitude between φ and $\varphi + d\varphi$ is proportional to $\sin \vartheta d\vartheta d\varphi$.

The distribution of rotational velocities needs a more extensive treatment. It will be recalled that, the Maxwellian distribution function for translational velocity as presented on pp. 93 to 110, is made up of independent factors, one for each degree of freedom. Grouped differently it consists first of a factor depending on the constants of the molecule and the temperature. This constant has such a value as to give the total number of molecules when the distribution function is integrated over all values of the coordinates. In case of a molecule which can move in three dimensions, this factor was $N_0\sqrt{m/2\pi kT^3}$. The last factor of the distribution function is the volume element of the three dimensional velocity space, and the middle factor is the expression $e^{-(u/kT)}$, where u means the total energy of the molecule. In the case of an infinitely high temperature this exponential function takes the value 1, and the relative

probability of different states is simply given by the relative size of the volume element $d\omega = d\xi d\eta d\zeta$ of the velocity space, which in turn is determined by the limits specified for the velocity under consideration.

In a similar manner the probability that the rotational velocity lies in a certain limited range will first be proportional to the volume element which gives this range. In a diatomic molecule there are two components of the rotational velocity as described before. Therefore, this volume element will be two dimensional; it will be the element of a "velocity surface." If for a given polar angle ϑ the angular velocity about the polar axis has a value between $\dot{\varphi}$ and $\dot{\varphi} + d\dot{\varphi}$, and simultaneously the angular velocity along the meridian has a value between $\dot{\vartheta}$ and $\dot{\vartheta} + d\dot{\vartheta}$ this surface element has the value $d\dot{\vartheta}$ $\sin \vartheta d\dot{\varphi}$.

If the temperature were infinite, this would give the probability of the rotational velocity apart from a constant factor made up so as to give the total number of molecules correctly. If the temperature is finite it is a most probable analogy to introduce here too a factor $e^{-(\epsilon_r/kT)}$ where ϵ_r means the rotational energy of the molecule (equation 208). This procedure is suggested clearly because, in the case of translation, the factor $e^{-(u/kT)}$ does not contain anything peculiar to translation but includes even the potential energy. However, a more complete demonstration can be given by continuing the reasoning which led to an exact proof of Maxwell's law for the velocity of translation (pp. 130 to 136). Let it be assumed that there are two kinds of molecules, one of which can only rotate around a fixed center while the other can have only translational motion. By calculating the changes which occur in the distribution of both kinds due to collisions between the two, one can show in exactly the same manner as that of the foregoing treatment that Maxwell's law holds as well for rotation as for translation.

In order to complete the expression it is only necessary to introduce a constant factor to take care of the total number of molecules. The number of molecules having, at a given moment, an orientation of their axes between the angles ϑ and $\vartheta + d\vartheta$, φ and $\varphi + d\varphi$ and, for their angular velocities, values between $\dot{\vartheta}$ and $\dot{\vartheta} + d\dot{\vartheta}$ and $\dot{\varphi}$ and $\dot{\varphi} + d\dot{\varphi}$, is then found to be

$$N_0 A e^{-\frac{\epsilon_r}{kT}} d\dot{\vartheta} d\vartheta \sin \vartheta d\dot{\varphi} \sin \vartheta d\varphi. \tag{210}$$

The constant A is evaluated in a manner exactly similar to that used in the case of pure translation. The total number of molecules is set equal to N_0. For the evaluation of the integral introduce $\Theta = \dot{\vartheta}$, $\Phi = \sin \vartheta \dot{\varphi}$ as the components of the angular velocity. Then the integral will take the form

$$N_0 = N_0 A \int_{-\infty}^{+\infty} e^{-\frac{I\Theta^2}{2kT}} d\Theta \int_{-\infty}^{+\infty} e^{-\frac{I\Phi^2}{2kT}} d\Phi \int_0^{\pi} \sin \vartheta d\vartheta \int_0^{2\pi} d\varphi. \tag{211}$$

The integration over the angles ϑ, φ gives 4π, the surface of a sphere of unit radius, the integration over the angular velocities is formally quite similar to

the integration over the transational velocity discussed previously, and leads to

$$\sqrt{\frac{2\pi kT}{I}}\sqrt{\frac{2\pi kT}{I}}. \tag{212}$$

This is equivalent to the two-dimensional translation case, the only difference being that the mass m, which is appropriate for the translational velocity, is replaced by the moment of inertia I, which is appropriate for rotation. Therefore, the final distribution formula for rotation takes the form

$$dN = N_0\left(\sqrt{\frac{I}{2\pi kT}}\right)^2 e^{-\frac{I}{2kT}(\dot{\vartheta}^2+\sin^2\vartheta\dot{\varphi}^2)}\,d\dot{\vartheta}\sin\vartheta d\dot{\varphi}\frac{\sin\vartheta d\vartheta d\varphi}{4\pi}. \tag{213}$$

The evaluation of the average kinetic energy can be written in exactly the same form as for the two-dimensional case of pure translation by using the previous substitution. Thus

$$\overline{u_r} = \left(\sqrt{\frac{I}{2\pi kT}}\right)^2\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{I}{2}(\Theta^2+\Phi^2)e^{-\frac{I}{2kT}(\Theta^2+\Phi^2)}\,d\Theta d\Phi = 2\frac{kT}{2}, \tag{214}$$

which gives accordingly to each of the two degrees of freedom of rotation an energy $RT/2$ per mol and a contribution to the molar heat capacity $R/2$, as would be the case for a degree of freedom of translation.

It will be seen from the following table that the molar heat capacities at constant volume of a number of the diatomic gases equal $5R/2$.

TABLE III[1]

	T° Abs.	C_v	
N_2	293	4.984	
	92	4.733	
O_2	293	4.985	
	197	4.83	Calculated value, $5R/2 = 4.95$
	92	4.91	
CO	291	5.006	
	93	4.758	

However, there are also obvious deviations in both directions.

	T° K.	C_v
H_2	288	4.875
	199	4.379
	92	3.335
Cl_2	291	5.90[2]

[1] K. Scheel and W. Heuse, *Ann. Physik*, **40**, 473 (1913).

[2] F. Voller, Diss., Berlin, 1908.

The experimental values which are lower than predicted can only be explained by means of the quantum theory. The high values for chlorine, on the other hand, suggest the possibility that some of the degrees of freedom have not been taken into account. Now a molecular model such as has been employed—known as the " dumb-bell " model since the two atoms act like masses at the end of a rigid rod—can rotate about the line joining the two atoms as well as about the two perpendicular axes about which the moment of inertia is I. This was originally assumed by Boltzmann [1] but, as a matter of fact, no such rotation takes place. The quantum theory is again required to prove this statement. It is, however, merely a generalization of the fact that the rotation of a *single* atom need not be taken into account, because the moment of inertia about the axis of the molecule is merely the sum of the moments of inertia of the individual atoms.

On the other hand, it must be remembered that the line connecting the two atoms is not rigid. The two atoms can therefore vibrate with respect to each other without affecting the motion of the center of gravity of the molecule. This means that the displacements of the two atoms from their equilibrium positions must always be oppositely directed, the two being at the same instant either both inside or both outside the positions of rest. Furthermore, the two displacements must be inversely proportional to the masses, and therefore directly proportional to the distances from the center of gravity, so that the various configurations of the molecule are always geometrically similar. If the total displacement is X,

$$X_1 = \frac{m_2}{m_1 + m_2} X; \qquad X_2 = \frac{m_1}{m_1 + m_2} X, \tag{215}$$

and there is obtained for the energy of vibration

$$\epsilon_\nu = \frac{m_1 m_2}{m_1 + m_2} \frac{1}{2} (\dot{X}^2 + 4\pi^2 \nu^2 X^2). \tag{216}$$

Thus the energy equation is identical with that for a single vibrating particle of mass $m_1 m_2/(m_1 + m_2) = \bar{m}$. If the two masses are very different this fraction is approximately equal to the smaller mass, because the larger body is almost at rest. This " relative mass " enters all problems of relative motion such as planetary motion about the sun or rather about the common center of gravity.

Consider now a diatomic molecule whose atoms can vibrate but whose center of gravity is fixed in space. In order to describe the state of this molecule completely it is necessary to know that the displacement at a given moment is between X and $X + dX$, and that the corresponding velocity is between $\dot{X}$ and $\dot{X} + d\dot{X}$. The state of the molecule may be described by a state point on a surface of coordinates X and $\dot{X}$. Then the foregoing conditions correspond to the requirement that the statepoints lie in the elementary area $dX d\dot{X}$.

[1] L. Boltzmann, *Wien. Ber.*, **63**, 397 (1871).

The number of molecules fulfilling this requirement is

$$dN = N_0 A' e^{-\frac{\epsilon_\nu}{kT}} d\dot{X} dX = N_0 A' e^{-\frac{\overline{m}\dot{X}^2}{2kT}} d\dot{X} e^{-\frac{4\pi^2\nu^2\overline{m}X^2}{2kT}} dX. \tag{217}$$

The factor A' is determined as before by putting the total number of molecules equal to N_0:

$$\left.\begin{aligned} N_0 &= N_0 A' \int_{-\infty}^{+\infty} e^{-\frac{\overline{m}}{2kT}\dot{X}^2} d\dot{X} \int_{-\infty}^{+\infty} e^{-\frac{4\pi^2\nu^2\overline{m}}{2kT}X^2} dX \\ &= N_0 A' \sqrt{\frac{2kT}{\overline{m}}} \int_{-\infty}^{+\infty} e^{-u^2} du \sqrt{\frac{2kT}{4\pi^2\nu^2\overline{m}}} \int_{-\infty}^{+\infty} e^{-v^2} dv, \end{aligned}\right\} \tag{218}$$

$$A' = \frac{1}{\pi \sqrt{\frac{2kT}{\overline{m}}} \sqrt{\frac{2kT}{4\pi^2\nu^2\overline{m}}}} = \frac{\nu\overline{m}}{kT}. \tag{219}$$

The average energy per mol is then given by the equation

$$\begin{aligned} \overline{U}_\nu &= N_A A' \int\int \epsilon_\nu e^{-\frac{\epsilon_\nu}{kT}} d\dot{X} dX \\ &= N_A A' \left[\int_{-\infty}^{+\infty} \frac{\overline{m}}{2} \dot{X}^2 e^{-\frac{m}{2}\frac{\dot{X}^2}{kT}} d\dot{X} \int_{-\infty}^{+\infty} e^{-\frac{\overline{m}}{2}\frac{4\pi^2\nu^2X^2}{kT}} dX \right. \\ &\quad \left. + \int_{-\infty}^{+\infty} e^{-\frac{\overline{m}}{2}\frac{\dot{X}^2}{kT}} d\dot{X} \int_{-\infty}^{+\infty} \frac{\overline{m}}{2} 4\pi^2\nu^2 X^2 e^{-\frac{\overline{m}}{2}\frac{4\pi^2\nu^2X^2}{kT}} dX \right], \end{aligned} \tag{220}$$

which has exactly the same form as the formula for the average energy of pure translation of a two-dimensional gas (104) $\dot{X}$ taking the place of ξ and $2\pi\nu X$ of η. The first member in (220) represents the kinetic energy, the second the potential energy. The integration is then performed in a similar manner and leads to the value

$$\overline{U}_\nu = RT,$$

where $RT/2$ is contributed by the average kinetic energy in the same way as it has been contributed by this kinetic energy in all the preceding cases, and $RT/2$ is contributed by the potential energy. It is well known that in the case of a vibrating system with elastic forces or of a simple pendulum, the average of the potential energy is equal to the average of the kinetic energy, each supplying half of the total energy. The contribution of the vibration to the specific heat is accordingly R calories per mol.

If the molecule is now permitted to have motions of translation and rotation besides vibration the formula giving the distribution law will be made up of independent factors, each referring to one degree of freedom, i.e., the number of molecules which lie at a certain moment in a volume element between x and $x + dx$, y and $y + dy$, z and $z + dz$; the velocity components of which lie between ξ and $\xi + d\xi$, η and $\eta + d\eta$, ζ and $\zeta + d\zeta$ while, at the same time

their axes have an orientation given by the ranges of angles ϑ to $\vartheta + d\vartheta$, φ to $\varphi + d\varphi$ and an angular velocity, the components of which lie between the limits $\dot{\vartheta}$ and $\dot{\vartheta} + d\dot{\vartheta}$, $\dot{\varphi}$ and $\dot{\varphi} + d\dot{\varphi}$, and finally, a vibration of the atoms such that at the same moment the displacement of the atoms is between X and $X + dX$, while they move relatively to each other with a velocity between $\dot{X}$ and $\dot{X} + d\dot{X}$; is given by

$$dN = N_0 \frac{dxdydz}{v} \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m}{2}\frac{\xi^2}{kT}} d\xi \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m}{2}\frac{\eta^2}{kT}} d\eta \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m}{2}\frac{\zeta^2}{kT}} d\zeta$$
$$\times \frac{\sin\vartheta d\vartheta d\varphi}{4\pi} \sqrt{\frac{I}{2\pi kT}} e^{-\frac{I}{2}\frac{\dot{\vartheta}^2}{kT}} d\dot{\vartheta} \sqrt{\frac{I}{2\pi kT}} e^{-\frac{I}{2}\frac{\sin^2\vartheta\dot{\varphi}^2}{kT}} \sin\vartheta d\dot{\varphi}$$
$$\times 2\pi\nu \sqrt{\frac{\overline{m}}{2\pi kT}} e^{-\frac{\overline{m}}{2}\frac{4\pi^2\nu^2X^2}{kT}} dX \sqrt{\frac{\overline{m}}{2\pi kT}} e^{-\frac{\overline{m}}{2}\frac{\dot{X}^2}{kT}} d\dot{X}. \quad (221)$$

Furthermore, the total average energy of a molecule is made up here by the sum of contributions of translation, rotation and vibration, just as in the case of a single atom it was made up of a sum of contributions from each degree of freedom of translation.

The justification for the integration to infinity in equations (214) and (218) is the same as on page 101, namely that due to the very strong decrease of the value of the exponential formula, it does not make any appreciable difference for the value of the integral if it is extended to a rather high upper limit or actually to infinity. The latter calculation is very much simpler than the former.

From equations (110), (214) and (218) it is apparent that the total molecular heat capacity at constant volume should be

$$\underset{\text{Translation}}{\frac{3}{2}R} + \underset{\text{Rotation}}{\frac{2}{2}R} + \underset{\text{Vibration}}{\frac{2}{2}R} = \frac{7}{2}R. \quad (222)$$

This value, however, is not attained by many diatomic gases at normal temperatures, the actual values being between $\frac{5}{2}R$ and $\frac{7}{2}R$. The reasons for this can only be obtained from the quantum theory.

The foregoing principles remain unchanged in the treatment of polyatomic gases, the only difference being a new, namely the third, axis of rotation so that the specific heat of rotation is $\frac{3}{2}R$.

There are, moreover, further possibilities for vibration. For example, the value of C_v for methane, CH_4, at 15° C. is 6.49. Since $3R = 5.94$, it is seen that the heat capacity is due to the translation and rotation and only slightly (0.55) to the vibration. Here again the anomaly can only be explained by the quantum theory. C_v for water vapor at 110° is 6.7, from which it may be deduced that three rotational degrees of freedom are present, that is, that the three atoms cannot lie in a straight line.

The Equilibrium of Dissociation: A kinetic model of the dissociation of a molecule will now be given. At the outset a greatly simplified picture will be employed but the simplifications will be successively removed in the course of the discussion.

Consider the dissociation equilibrium of a diatomic molecule;

$$M_{\text{I-II}} \rightleftharpoons A_{\text{I}} + A_{\text{II}} \tag{223}$$

and make the following preliminary picture: Each atom I is surrounded by a spherical shell of radius d and thickness δ, small compared with d. The volume of this shell is $4\pi d^2\delta$. Two atoms I and II are said to be combined in one molecule if the center of II is contained in the shell surrounding atom I. Any atom II whose center is not contained in some shell is said to be free; any atom I having no center of an atom II in its shell is considered a free atom I. Each of the shells around atom I can contain only one center of an atom II. The next simplification is to assume that there are no forces between the atoms I and II. In other words the heat of dissociation of the molecule is zero. The number of free atoms I will be denoted by N_{I}; the number of free atoms II by N_{II}; the number of molecules by N_M and the total volume by v. Then the ratio of the free atoms II to the atoms II in combination with atoms I will be given by the ratio of the space available for free atoms II, which is the total volume, v, to the space available for the formation of molecules

$$4\pi d^2\delta N_{\text{I}}. \tag{224}$$

Actually the total volume minus the volume of the shells should have been written for the volume available to free atoms, but if the total volume is large enough to consider the gases in the mixture as ideal, the difference can be neglected. The expression of the mass action law is therefore found to be $N_{\text{II}} : N_M = v : 4\pi d^2\delta N_{\text{I}}$ or

$$\frac{N_{\text{II}}}{vN_M} N_{\text{I}} = \frac{1}{4\pi d^2\delta} \tag{225}$$

or

$$\frac{C_{\text{I}}C_{\text{II}}}{C_M} = K_0 = \frac{1}{N_A 4\pi d^2\delta}. \tag{226}$$

This agrees with the result of the formal thermodynamic treatment in the way in which the concentrations enter. It is also in agreement in that K_0 is independent of the temperature as should be the case if the heat of reaction is zero.

The kinetic treatment, however, goes further than pure thermodynamics by giving the numerical value of the constant in terms of molecular data. To evaluate the order of magnitude of K_0 it might be assumed that

$$d = 3 \times 10^{-8} \text{ cm.}, \qquad \delta = 10^{-9} \text{ cm.}$$

If the unit of concentration is mols per liter, the constant K_0 is found to equal $\frac{1}{6} \cdot 1000 = 150$.

The next step is to assume that when an atom II enters the shell of an atom I the potential energy of the two decreases by an amount Q_0/N_A. In other words, there is now a heat of dissociation equal to Q_0 calories per mol and independent of the temperature. According to Kirchhoff's Law, this latter fact means that no change in specific heat is involved in the formation of the molecule. In fact, according to our model, atom I even when combined retains its full share of thermal energy which is entirely translational and equal to $3RT/2$. The same is true of atom II, which can move inside the shell as freely as when outside, except for the fact that the space is limited. The molecule would then have a specific heat $C_v = 6R/2$. With this new model the only change is to increase the probability of an atom II being inside the shell by a factor $e^{Q_0/RT}$. Then the previous reasoning leads to a mass action law of the form

$$\frac{C_{\mathrm{I}}C_{\mathrm{II}}}{C_M} = K = K_0 e^{-Q_0/RT}. \tag{227}$$

As in the previous case, this expression is in agreement with thermodynamics with respect to the dependence on concentration and temperature, since now

$$\frac{\partial ln K}{\partial T} = \frac{Q}{RT^2}. \tag{228}$$

Here again the kinetic treatment gives in addition the numerical value of the constant factor K_0.

The next and final step [1] is necessary to obtain the correct specific heat for the model of the molecule. According to classical theory this is $C_v = 7R/2$. For this purpose it can no longer be assumed that the atom II can move freely inside of the shell of an atom I, work only being done if it passes the outside border of the shell, but rather must it be assumed that the atom II is bound elastically within the shell. Accordingly, not all places inside the shell are equally probable, and the total probability that the center of an atom I shall be inside the shell, is not given simply by the ratio of the volume of this shell to the total volume. Assume that the center of the atom II would be in equilibrium anywhere on the surface of a sphere of radius r_0 circumscribed about the center of the atom I. Let Q_0 equal the difference of potential calculated per mol between an atom II in this position, and a free atom II. Assume, furthermore, that the center of the atom II is bound to this position by a radial quasi-elastic force given by $-4\pi^2\nu^2\overline{m}(r - r_0)$, where ν is the frequency of the free oscillation of II about the equilibrium position, and $r - r_0$ is the deviation from this position. Then the relative probability that the center of a bound atom will lie within a shell of inner radius r and outer radius $r + dr$

[1] L. Boltzmann, Vorlesungen uber Gastheorie, V. II, p. 177; O. Stern, *Ann Physik*, **44**, 497 (1914); K. F. Herzfeld, *Physik. Z.*, **22**, 186 (1921); **23**, 95 (1922); *Ann. Physik*, **69**, 54 (1922); P. Ehrenfest und V. Trkal, *Ann. Physik*, **65**, 609 (1921); R. H. Fowler, *Phil. Mag.*, **45**, 1 (1923); Statistical Mechanics, Cambridge, 1929, pp. 100 ff.; C. G. Darwin and R. H. Fowler, *Proc. Camb. Phil. Soc.*, **21**, 730 (1923).

is given by

$$e^{-\frac{\overline{m}}{2kT}4\pi^2\nu^2(r-r_0)^2}4\pi r^2 dr. \tag{229}$$

The relative probability that the center of this atom II will lie within a particular element of the shell described as above, rather than outside will be given by the ratio

$$e^{-\frac{Q_0}{RT}}e^{-\frac{\overline{m}}{2kT}4\pi^2\nu^2(r-r_0)^2}4\pi r^2 dr : v \tag{230}$$

and, accordingly, the relative probability that the center of an atom II will lie anywhere within any of the shells compared with the probability that it will lie in free space, or the ratio of the number of combined atoms II to free atoms II will be given by

$$\left.\begin{aligned} N_M : N_{II} &= N_I e^{\frac{Q_0}{RT}}\int e^{-\frac{\overline{m}}{2kT}4\pi^2\nu^2(r-r_0)^2}4\pi r^2 dr : v \\ &= N_I e^{\frac{Q_0}{RT}}4\pi r_0^2\sqrt{\frac{2\pi kT}{4\pi^2\nu^2\overline{m}}} : v \\ &= N_I e^{\frac{Q_0}{RT}}\frac{2r_0^2}{\nu}\sqrt{\frac{2\pi kT}{\overline{m}}} : v \end{aligned}\right\} \tag{231}$$

or

$$\frac{C_I C_{II}}{C_M} = K = \frac{\nu}{2N_A r_0^2}\sqrt{\frac{\overline{m}}{2\pi kT}}e^{-\frac{Q_0}{RT}}. \tag{232}$$

On comparing this with equations (226) and (227), it is seen that the fixed thickness δ of the former shell has been replaced by an average thickness $\frac{1}{\nu}\sqrt{\frac{kT}{2\pi\overline{m}}}$ proportional to the average amplitude of the vibration, and accordingly, proportional to the square root of the temperature. The order of magnitude of the new expression is, for normal conditions, not much different from the value calculated before, but there is now a dependence on the temperature. Since

$$\left.\begin{aligned} \frac{\partial \ln K}{\partial T} &= \frac{\partial}{\partial T}\left(-\frac{Q_0}{RT}-\frac{1}{2}\ln T\right) \\ &= \frac{Q_0-\frac{1}{2}RT}{RT^2} \\ &= Q/RT^2, \end{aligned}\right\} \tag{233}$$

it appears that the heat of reaction is no longer constant. According to thermodynamics, this means that the sum of the specific heats of the free atoms is smaller than the specific heat of the molecules by the amount $R/2$, while in the previous case they were equal. The introduction of the quasi-elastic force with its potential energy has increased the specific heat of the molecules from $6R/2$ to $7R/2$. This new formula is identical not only in the way in which it depends

on temperature and concentration, but also in the numerical factors obtained from the application of Nernst's heat theorem to the thermodynamical formula of equilibrium. In fact the kinetic development gives the theoretical evaluation of the chemical constants, and explains the fact that all these are of the same order of magnitude by the fact that the molecular dimensions (the size of the shell) are of the same order of magnitude for the different molecules.

The formula which has been deduced contains also a kinetic explanation of the Braun-Le Chatelier principle in its narrower sense, (cf. Chap. VIII). The effect of the temperature will be first investigated. For this the exponential term is the determining factor. This favors that state, or more exactly, those positions of the atoms toward which the forces act, or in other words those positions whose attainment is accompanied by the production of energy. On the other hand the kinetic energy of the gas tends to produce a uniform distribution of atoms. At low temperatures the effect of the exponent is increased and that of the kinetic energy decreased. With decreasing temperature, therefore, the forces promote more and more the formation of those compounds which are formed with evolution of heat. At higher temperatures, the distribution of the atoms approaches uniformity throughout the space. Generalizing this result in an approximate manner a meaning can now be given [1] to the statement that " the formation of endothermic compounds (those which take up heat of formation) is favored by high temperatures," that is, it can now be stated *to what extent* the formation is favored. Consider a reaction in which the molecules I, II . . . react to form the molecules I', II'. . . . The atoms A, B, C . . . occur in the molecules and there are the same number of atoms A on each side of the stoichiometric equation. The atoms A are, however, present in different types of molecules on the two sides of the equation. At sufficiently high temperatures the heat of reaction plays no role because $e^{-(Q_0/RT)} \sim 1$. The only determining factor for the equilibrium constant is then the volume relationships between the reactants and the products. The entire volume v is available for *one* atom of each molecule, corresponding to the transational motion of the whole molecule. The motion of all the other atoms of this molecule is limited to the immediate neighborhood of the first atom, i.e. to a volume $\tilde{v}_1$ of molecular dimensions. If there are a molecules of reactants and b molecules of products and t is the total number of atoms appearing on either side of the stoichiometric equation, the mass action expression becomes

$$\frac{N_{\mathrm{I}} N_{\mathrm{II}} \ldots N_a}{N_{\mathrm{I}}' N_{\mathrm{II}}' \ldots N_b} = - \frac{V^a \tilde{v}_1 \ldots \tilde{v}_{t-a}}{V^b \tilde{v}_1 \ldots \tilde{v}_{t-b}} \tag{234}$$

because, for example in the reactant, a atoms, one in each of the a molecules, can chose their places anywhere in the volume v, while all the remaining $t-a$ atoms are then bound to the small volumes $\tilde{v}$ in the immediate neighborhood of the atoms mentioned first. Since all of the $\tilde{v}$'s are of the same order of magnitude, the equilibrium constant is determined by the numbers a and b; the right hand side of the equation is approximately $V^{a-b}\tilde{v}^{b-a}$ or, if the con-

[1] K. F. Herzfeld, *Physik Z.*, **23**, 95 (1922).

centrations are expressed in mols/cc, $K \sim (1/2)^{a-b}$ (cf. p. 146) or again, if the unit of concentration is taken as that of a gas at 0°C. and 1 atmosphere, $10^{4(a-b)}$. Thus, the direction of the reaction which causes the formation of the most molecules is favored by a factor of 10^4 for each molecule formed in excess of the molecules consumed. If the number of molecules of reactants equals the number of molecules of products, the spaces available for the two are nearly equal and, at sufficiently high temperatures, the equilibrium constant is of the order of magnitude unity. If the temperature decreases, the constant shifts, in accordance with the barometric formula, with the factor $e^{Q_0/RT}$, which forces many more atoms to positions of low energy content (that is, into compounds which give out considerable heat in their irreversible formation). The exponential then predominates over the volume conditions.

However, the agreement between the results of the kinetic treatment and those of thermodynamics is more than qualitative in this general case as well as before for the diatomic molecule. The relation known as the van't Hoff reaction isochore is deduced in thermodynamics:[1]

$$\frac{\partial ln K_c}{\partial T} = -\frac{Q}{RT^2}. \tag{235}$$

According to the First Law, Q may be replaced by $Q_0 - \sum C_v T$ (in the case of gases; the individual summands are taken positive for the left and negative for the right hand side of the reaction equation). Integration of this equation gives the result

$$ln K_c = \frac{Q_0}{RT} + \sum \frac{C_v}{R} ln T + \sum j'', \tag{236}$$

where the j'''s differ from the so-called chemical constants only in that the present equation gives K_c instead of K_p and contains natural instead of base 10 logarithms ($j'' = j/0.4343 - lnR$).

Therefore

$$K_c = e^{Q_0/RT} \frac{\text{Product of } (e^{j''} . T^{C_v/R}) \text{ for all molecules on left}}{\text{Product of } (e^{j''} . T^{C_v/R}) \text{ for all molecules on right}}. \tag{237}$$

This expression is in exact agreement with the formula obtained from the kinetic treatment. It will be noticed that the dependence of the equilibrium constant upon the specific heat, as expressed by the terms in $T^{C_v/R}$, gives the relative increase with temperature of the integral of state (the space v increases with rising temperature more rapidly for the molecule with the greatest specific heat and such a molecule is therefore favored), while $e^{j''}$ is responsible for the absolute value.

There is still to be given the proof of the other statement of the Braun-LeChatelier Principle to the effect that if the volume of the system is decreased that direction is favored which (under the same conditions, e.g., constant pressure) assumes the smaller volume. In other words, that direction of the reaction is favored in which the smallest number of gaseous molecules is formed.

[1] Chap. VIII.

For example, in the reaction

$$2H_2 + O_2 \rightleftharpoons 2H_2O,$$

the forward reaction is favored. This is caused by the fact that if the volume is decreased, the space available for the independent atoms II (for example, the dissociation HBr = H + Br, in which the hydrogen atom will be designated as atom II) is decreased while the space available to the combined atoms of type II is not decreased, since the latter is simply the volume of the spherical shells circumscribed about the bromine atoms. The space available for the bromine atoms changes, of course, for the free atoms and for those considered as molecular kernels in the same way. If the number of free hydrogen atoms remained unchanged, their concentrations would increase. The concentration of the combined hydrogen atoms, however, remains unchanged, so that the concentration ratio is no longer satisfied, with the result that the degree of dissociation is decreased.

It is essential to the entire calculation that it is unnecessary to take account of the orientation (rotation) of the *atoms* either in the free or in the combined state.

The Velocity of Dissociation: An attempt will now be made to deduce the equation for the velocity of dissociation of a gas consisting of diatomic molecules. Let Q_1 equal the heat of dissociation and assume that the quasi-elastic forces holding the atoms together extend to a separation equal to X_0 at which distance the potential energy

$$\frac{m}{2}(2\pi\nu)^2 X_0^2$$

equals the heat of dissociation (per molecule) Q_1/N_A and that upon further separation the molecule dissociates. The problem is now to determine how many times this happens per second per N_A molecules. To do this it is most convenient to employ the $X - \xi$ phase plane whereupon it becomes a question of how many statepoints cross the line $X = X_0$ per second.[1] The velocity of the statepoints perpendicular to the " molecular limit " $X = X_0$ is ξ, (that is, the velocity in the X-direction, $dx/dt = \xi$). The number of molecules transgressing this limit (X_0) in unit time is the density of statepoints at the limit,

$$N_A \frac{e^{-\frac{m}{2}\frac{(2\pi\nu)^2 X_0^2}{kT}} e^{-\frac{m}{2}\frac{\xi^2}{kT}}}{\int_{-\infty}^{+\infty} e^{-\frac{m}{2}\frac{(2\pi\nu)^2 X_0^2}{kT}} dX \int_{-\infty}^{+\infty} e^{-\frac{m}{2}\frac{\xi^2}{kT}} d\xi}, \tag{238}$$

multiplied by ξ and integrated with respect to ξ from 0 to ∞ (not from $-\infty$ to $+\infty$ because only passages across the limit from left to right are of interest).

[1] A similar presentation was first given by A. Marcelin, *Ann. chim. phys.*, (9) **3**, 120, 185 (1915); cf. also A. March, *Physik. Z.*, **18**, 53 (1917).

Therefore,[1]

$$\left.\begin{aligned} k_1 &= N_A \frac{e^{-\frac{Q_1}{RT}}}{\int_{-\infty}^{+\infty} e^{-\frac{m}{2}\frac{(2\pi\nu)^2}{kT}X^2}} dX \frac{\int_0^{\infty} \xi e^{-\frac{m}{2}\frac{\xi^2}{kT}} d\xi}{\int_{-\infty}^{+\infty} e^{-\frac{m}{2}\frac{\xi^2}{kT}} d\xi} \\ &= \frac{N_A e^{-\frac{Q_1}{RT}}}{\sqrt{\frac{2\pi kT}{m}}\frac{1}{2\pi\nu}} \cdot \frac{\frac{1}{2}\frac{2kT}{m}}{\sqrt{\frac{2\pi kT}{m}}} = N_A \nu e^{-\frac{Q_1}{RT}}. \end{aligned}\right\} \quad (239)$$

This means that the atoms $N_A e^{-\frac{Q_1}{RT}}$ whose vibrational energy is sufficient for dissociation to take place, have an average life equal to $1/\nu$.[2] The correct value for the equilibrium constant is obtained from k_1 and k_2, the velocity constant of the reverse reaction, namely, the formation of molecules (cf. Chap. VIII), if it is assumed that every collision between two atoms results in the formation of a molecule, namely, that $k_2 = k_2^0$. This is in conformity with the calculation of the velocity of dissociation since it was assumed in that calculation that each time the center of an atom transgresses the molecular limit a molecule dissociates. Similarly, the velocity of recombination was calculated with the assumption that two atoms combine if their centers approach to within the normal distance between their centers when combined.[3] Actually this is often not true. If only a fraction combines, the same factors must be applied to the dissociation.

THE PHENOMENA OF FLOW AND CONDUCTION

The laws of viscosity, heat conduction and diffusion have afforded, in their time, much important evidence in support of the kinetic theory. Their fundamental features may be readily and simply deduced. It must be realized, however, that the developments of this section are not correct in so far as they do not take into account the disturbance of the distribution of the molecular velocities due to the flow and other factors. This omission can be avoided, in general, according to the methods outlined on pp. 130–137, but the calculations are usually very difficult. In most cases such a detailed development does not affect the qualitative results of the simpler approximate method and has merely the effect of altering the numerical value of some coefficient. In a few instances, however, the more exact calculation shows that some coefficient is zero, which would otherwise have been given a finite value. In such

[1] In the denominator it is permissible to carry the integration with respect to X to ∞ if $Q_1/RT \gg 1$.

[2] It has been assumed in this treatment that only vibrational energy causes dissociation.

[3] K. F. Herzfeld, *Ann. Physik*, **59**, 635 (1919); E. K. Rideal, *Phil. Mag.*, **40**, 461 (1920); S. Dushman, *J. Am. Chem. Soc.*, **43**, 397 (1921).

In fact, k_1 was first calculated by reversing this reasoning.

instances even the qualitative predictions of the inexact development are in error (e.g., p. 188, note 1).

Viscosity of Gases at Medium Pressures: Consider a layer of gas of thickness d and extending to infinity on all sides. This layer is bounded by two plane surfaces parallel to the XY plane. The lower surface ($z = 0$) is stationary and the upper ($z = d$) is moving in the direction of the X-axis with the velocity W_0. Experiment shows that in the stationary state the following conditions are fulfilled. The gas sticks to the two surfaces, if its density is not too small, so that at the bottom surface its velocity is zero and at the upper its absolute velocity is W_0 in the X-direction. At the height z the velocity of the gas equals $\frac{z}{d} W_0$. Each infinitely thin sheet of gas moves along the X-axis in its proper plane, the higher the sheet the greater being its velocity. This motion of the gas is caused by its internal friction. That is, each layer of the gas attempts to drag along with it the layer next below and to retard the layer immediately above. These frictional forces are also exerted on the enclosing surfaces. The force per square centimeter required to keep the bottom surface at rest or, which is the same thing, to keep the upper surface in uniform motion is given by

$$\eta \frac{\partial W}{\partial z} = \eta \frac{W_0}{d}, \tag{240}$$

where η is the coefficient of viscosity and has the dimensions $\mathrm{gm} \times \mathrm{cm}^{-1} \times \mathrm{sec}^{-1}$. A kinetic explanation is now to be sought for the force which is exerted on each layer of the gas by the neighboring layers.

Throughout the present discussion the velocity of flow W will be defined at that velocity which must be subtracted from the X-component of the total velocities of the molecules in order that the remaining velocities shall be distributed according to Maxwell's Law. The remaining velocities will accordingly define the temperature.[1]

Consider any layer at the height z, in which the velocity of flow $W = W_0 \frac{z}{d}$. The friction force exerted in the X-direction on this layer may be determined by calculating the amount of momentum in the X-direction transported upward in unit time through 1 sq. cm. of the layer. It will again be assumed as on p. 77 that 1/3 of all the molecules are moving in the vertical direction. Of these, one half are moving upwards and the other half downwards. If the number of molecules per cubic centimeter is designated, as usual, by N_A/V, there are $\frac{N_A}{6V} |\overline{w}|$ molecules[2] crossing each square centimeter of the upper boundary of the layer per second coming from above. Aside

[1] J. C. Maxwell, *Phil. Mag.*, **19**, 31 (1860). This is not quite correct. See pp. 130–138.

[2] $|\overline{w}|$ is the magnitude of the average molecular velocity.

from their thermal velocity these molecules possess an additional velocity in the X-direction, W_+, which is greater than that possessed by the molecules of the layer under consideration. This is because the last opportunity that each molecule coming from above had to adjust its velocity was at its last collision, which was, on the average, at a distance equal to one mean free path Λ above the layer z. On the average, therefore, each molecule assumed at its last collision the velocity of flow prevailing in the layer in which the last collision occurred, namely, the velocity of the layer $z + \Lambda$. This velocity equals

$$W_+ = W + \frac{\partial W}{\partial z}\Lambda. \tag{241}$$

The higher terms of this Taylor's series are neglected, corresponding to the assumption of a linear velocity gradient expressed by equation (240). The molecules coming from above therefore bring into the layer an amount of momentum in the X-direction equal to

$$\frac{N_A}{6V}|\overline{w}|\, mW_+, \tag{242}$$

since each molecule carries an X-component of momentum of mW_+.

Similarly the molecules coming upwards from the layer below have a velocity equal to

$$W_- = W - \frac{\partial W}{\partial z}\Lambda \tag{243}$$

because they come from a layer lower by the distance Λ. They carry upwards an X-component of momentum equal to

$$\frac{N_A}{6V} \cdot |\overline{w}| \cdot mW_-. \tag{244}$$

The net flow of momentum through the layer is therefore

$$\frac{N_A}{6V}|\overline{w}|\, m(W_+ - W_-) = \frac{N_A}{3V}|\overline{w}|\, m\Lambda \frac{\partial W}{\partial z}. \tag{245}$$

This excess momentum is due to the fact that molecules moving downward have a larger X-component of velocity than those coming from beneath.

This downward flow of momentum along the X-axis corresponds to a force acting on the lower limiting surface, the value of this force per square centimeter being

$$\frac{N_A}{3V}|\overline{w}|\, m\Lambda \frac{\partial W}{\partial z}. \tag{246}$$

Upon comparison with equation (240) it is seen that

$$\eta = \frac{N_A}{3V}|\overline{w}|\, m\Lambda = 1/3\ M|\overline{w}|\, c\Lambda, \tag{247}$$

where M is the molecular weight and c is the number of mols per cc. Before proceeding to the discussion of this equation the fundamental facts may be summarized as follows: The effect experienced by any layer of the gas due to the layer immediately above it is caused by the downward migration of molecules from the upper layer. These molecules are moving faster in the direction of the X-axis than are the molecules of the first layer. Upon collision, the differing amounts of momentum are exchanged so that the first layer is accelerated in the X-direction. On the other hand, the slower molecules coming upwards from the layer immediately below the layer under consideration tend to retard the latter. In the stationary state the acceleration and retardation compensate each other. The excess components of velocity in the X-direction are changed by collisions to velocities in which no direction is favored; the mass motion of the molecules is partly converted into thermal motion: as a result of its viscosity, the gas is warmed.[1] The force exerted upon the lower surface is caused by the fact that the molecules reaching it still have an excess momentum in the X-direction which they give up to the plate upon collision. After the subsequent reflection they retain only their thermal velocity. This force caused by collisions is along the X-axis and therefore in the plane of the plate, and must be balanced by an external force to preserve equilibrium. There is a point to be noted in this connection which will be brought up later (p. 159).

To return to equation (247), it is seen that the viscosity of a gas is *independent of the density*, since Λ is inversely proportional to c. This unexpected result was first deduced from the theory by Maxwell. After the experimental confirmation by Kundt and Warburg it became one of the strongest pieces of evidence in support of the kinetic theory[2] (Table IV). The reason for this independence of density is that, although the number of molecules acting as carriers of momentum is increased by increase in the density, at the same time the effect of each carrier is diminished, since each one brings in a smaller excess (or deficiency) of momentum because it comes from a shorter distance.

TABLE IV

Apparent[3] Viscosity of Air at Different Pressures, $t = 15°$ C.

p, mm. Hg.	$\eta/\eta_{750\text{ mm.}}$	Λ (mm.)
750	1	6.0×10^{-5}
380	1.01	1.2×10^{-4}
20.5	1.004	2.2×10^{-3}
2.4	0.978	1.9×10^{-2}
1.53	0.956	0.030
0.63	0.908	0.073

Distance between the plates = 1.967 mm.

[1] G. Jäger, Winckelmanns Handb. d. Physik, Vol. III, p. 139 f., 2 ed., Leipzig, 1906.

[2] O. E. Meyer, *Pogg. Ann.*, **125**, 177 (1865); **127**, 253, 353 (1866); **148**, 1 (1873); O. E. Meyer and Springmühl, *Pogg. Ann.*, **148**, 526 (1873); Clerk Maxwell, *Phil. Trans.*, **156**, 249 (1866); W. Crookes, *Phil. Trans.*, **172**, 387 (1881).

[3] "Apparent" because the decrease at low pressures is caused by slippage.

The coefficient of viscosity should change with the temperature, according to (247), only in so far as $|\overline{w}|$ changes with the temperature. In other words, it should be proportional to $\sqrt{T}$ (because the velocity of transport is increased). Actually it increases with the temperature more rapidly than this. It may therefore be concluded that the mean free path increases with the temperature. The experimental data are in good agreement with the relation developed on p. 126, as is shown in Table V.[1] Nevertheless at low temperatures there appear deviations [2] of such a nature as would be caused by a decrease in Sutherland's constant C (p. 87) at these low temperatures. At very low temperatures (15–20° K.) Gunther [3] has shown that the Sutherland formula does not represent the experimental facts. Under these conditions the appropriate relation is $\eta \propto T^{3/2}$.

TABLE V

Viscosity of Air at Different Temperatures

$t°$ C.	$\eta \times 10^7$ obs.	$\eta \times 10^7$ calc.
−21.4	1639	1623
+15.0	1807	1810
99.1	2203	2204
182.4	2559	2552
302.0	2993	2997

The calculated values were obtained from Sutherland's formula using the value $C = 119.4$.

All the quantities of equation (247) are known with the exception of Λ. (The numerical factor 1/3 is not quite correct, see the following paragraph.) Viscosity measurements may therefore be used to calculate the value of the mean free path, and from this the diameter of the molecule (equation (131)). Thus Smith [4] has shown that nitrogen has the same viscous properties as carbon monoxide. Each of these gases is diatomic and each has the same molecular weight and number of electrons. (Isosterism of Langmuir. See Chapter V.) The same similarity holds for carbon dioxide and nitrous oxide which also show the same viscosity. Rankine [5] has compared the molecular dimensions of carbon oxysulphide obtained from viscosity measurements with dimensions calculated from model considerations.[6]

According to Enskog and Chapman (*loc. cit.*) [7] the accurate formulae are as follows:

For elastic spheres:

$$\eta = \frac{5}{16} \times 1.016 \sqrt{\frac{RTM}{\pi}} \frac{1}{N_A d^2} \tag{248}$$

[1] P. Breitenbach, *Ann. Physik*, **5**, 166 (1901). Cf. A. O. Rankine, *Proc. Roy. Soc.*, **111A**, 219 (1926); **117A**, 245 (1927).

[2] H. Vogel, *Ann. Physik*, **43**, 1235 (1914).

[3] P. Gunther, *Z. physik. Chem.*, **110**, 626 (1924).

[4] C. J. Smith, *Proc. Phys. Soc.*, **34**, 155 (1922).

[5] A. O. Rankine, *Phil. Mag.*, **44**, 292 (1922).

[6] Cf. also E. Mack, Jr., *J. Am. Chem. Soc.*, **47**, 2468 (1925).

[7] Cf. also H. R. Hassé and W. R. Crook, *Phil. Mag.*, [7] **3**, 977 (1927).

or with

$$\Lambda = \frac{1}{\sqrt{2}\pi c N_A d^2}, \tag{250}$$

and

$$|\overline{w}| = 2\sqrt{\frac{2RT}{\pi M}}, \tag{251}$$

$$\eta = 0.499 c M |\overline{w}| \Lambda. \tag{252}$$

If the elastic spheres attract each other according to the law of force, $F = A/r^n$, Sutherland's constant (equation (165)) becomes

$$C = \frac{217}{615} \cdot \frac{A}{k(n-1)d^{n-1}} \cdot \beta, \tag{253}$$

where β, the numerical coefficient has the following values:

$n =$	3	4	5	7	9
$\beta =$	0.701	0.636	0.587	0.517	0.467

Finally, if the molecules are assumed to be force centers repelling each other with forces proportional to A/r^n, instead of elastic spheres (p. 127), equation (248) is to be multiplied by the term $3\left(\frac{2kT}{A}\right)^{\frac{2}{n-1}}$ and also by a numerical factor dependent on n.[1]

The viscosity of gaseous mixtures is given by a rather complicated relation, but the approximate calculation may be carried through exactly as in the case of a simple gas. Thus the transport of momentum takes place in part through $N_A c_1$ molecules of the first kind and partly through $N_A c_2$ molecules of the second kind, etc. The molecules I have a free path Λ_1 and so forth. There is obtained in this manner the relation

$$\eta = 1/3\left[c_1|\overline{w}_1| m_1 \Lambda_1 + c_2 m_2 |\overline{w}_2| \Lambda_2 + \cdots\right] N_A. \tag{254}$$

If there are only two components in the mixture this becomes, upon inserting the values of Λ_1, Λ_2 given by (145) ($d = (d_1 + d_2)/2$),

$$\left.\begin{aligned}\eta = \frac{2\sqrt{2}}{3}\sqrt{\frac{RT}{\pi}}\frac{1}{N_A}\Bigg(&\frac{c_1\sqrt{M_1}}{\pi\sqrt{2}c_1 d_1^2 + \pi c_2 d^2\sqrt{\dfrac{M_1+M_2}{M_2}}} \\ &+ \frac{c_2\sqrt{M_2}}{\pi\sqrt{2}c_2 d_2^2 + \pi c_1 d^2\sqrt{\dfrac{M_1+M_2}{M_1}}}\Bigg)\end{aligned}\right\} \tag{255}$$

$$= \frac{\eta_1}{1 + \dfrac{c_2}{c_1}\left(\dfrac{d}{d_1}\right)^2\sqrt{\dfrac{M_1+M_2}{2M_2}}} + \frac{\eta_2}{1 + \dfrac{c_1}{c_2}\left(\dfrac{d}{d_2}\right)^2\sqrt{\dfrac{M_1+M_2}{2M_1}}}.$$

[1] For the evaluation of some of the integrals occurring in the expressions for viscosity, etc., as a function of the exponent n of the law of force see S. Chapman, *Mem. Proc. Manchester Lit. Phil. Soc.*, **66**, 1 (1922).

A formula of the type

$$\eta = \frac{\eta_1}{1 + \frac{c_2}{c_1}\beta_1} + \frac{\eta_2}{1 + \frac{c_1}{c_2}\beta_2} \tag{256}$$

has been obtained by Sutherland [1] with the aid of simplifying assumptions but taking into account his temperature correction. However, the same has been done independently by Theissen [2] with another meaning for β. These formulae are in good agreement with the experimental data.[3]

On the other hand the relation

$$\frac{\beta_1}{\beta_2} = \frac{\eta_1 M_2}{M_1 \eta_2}, \tag{257}$$

which follows from the equation deduced above is either not followed at all or at best only qualitatively.

If gas I is present in large excess over gas II, then

$$\eta = \eta_1 + \frac{c_2}{c_1}\left(\frac{\eta_2}{\beta_2} - \eta_1\beta_1\right).$$

In this case it can happen that, even if gas II has the smaller viscosity, ($\eta_2 < \eta_1$), the viscosity of the mixture may exceed that of gas I $\left(\frac{\eta_2}{\beta_2} > \eta_1\beta_1\right)$.[4]

A formula obtained by Puluj (*loc. cit.*) by using the average values of the molecular weights, velocities and cross sections in the simple equation, does not agree well with experiment.

Finally Maxwell [5] has deduced an accurate formula for the case of his special law of force K/r^5. This formula may be brought to the form

$$\eta = \frac{\eta_1}{1 + \frac{c_2}{c_1}\beta_1} + \frac{\eta_2}{1 + \frac{c_1}{c_2}\beta_2} + \frac{A}{\left(1 + \frac{c_2}{c_1}\beta_1\right)\left(1 + \frac{c_1}{c_2}\beta_2\right)}. \tag{258}$$

A only vanishes if the magnitude, which plays the role of mean free path in this theory, were connected in a certain hypothetical way with the corresponding magnitudes of the pure constituents. Furthermore, the β's of this formula have a meaning different from that in (256). Enskog gives the exact formula

[1] W. Sutherland, *Phil. Mag.*, (V) **40**, 421 (1895).

[2] M. Theissen, *Verh. deut. physik. Ges.*, **4**, 348 (1902).

[3] K. Schmitt, *Ann. Physik*, **30**, 393 (1909), and previous papers cited there.

[4] T. Graham, *Phil. Trans.*, **136**, 622 (1846); J. Puluj, *Wien. Ber.*, **79**, 97, 745 (1879); P Breitenbach, *Wied. Ann.*, **67**, 803 (1899); P. Tänzler, *Verh. deut. physik. Ges.*, **8**, 222 (1906).

[5] Clerk Maxwell, *Phil. Mag.*, (IV) **35**, 212 (1868); *Scient. Pap.*, **2**, 72.

$$\eta = \frac{\eta_1\left(1+\frac{c_1}{c_2}\beta_2\right)+\eta_2\left(1+\frac{c_2}{c_1}\beta_1\right)+A}{\left(1+\frac{c_1}{c_2}\beta_2\right)\left(1+\frac{c_2}{c_1}\beta_1\right)-\frac{A^2}{4\eta_1\eta_2}},$$

which differs from Maxwell's expression by the term $A^2/4\eta_1\eta_2$ in the denominator. For elastic spheres without attractive forces the constants have the values

$$\beta_1 = \frac{1}{12}\left(\frac{d_1+d_2}{d_1}\right)^2\sqrt{\frac{2m_2}{m_1+m_2}}\,\frac{5m_1+3m_2}{m_1+m_2}, \tag{260}$$

$$\beta_2 = \frac{1}{12}\left(\frac{d_1+d_2}{d_2}\right)^2\sqrt{\frac{2m_1}{m_1+m_2}}\,\frac{3m_1+5m_2}{m_1+m_2}, \tag{261}$$

$$A^2 = 16\eta_1\eta_2\beta_1\beta_2\frac{m_1m_2}{15m_1^2+34m_1m_2+15m_2^2}.^{1} \tag{262}$$

Viscosity at Low Density. Slippage: It was found by Kundt and Warburg[2] that, at very low pressures, the apparent viscosity decreases with the pressure. (Cf. Table IV, p. 155.) From this fact they deduced that under these conditions the gas no longer sticks to the moving surface, but slips along it, that is, the layer of gas next to the surface has a velocity of flow different from that of the surface. The relation becomes especially simple if the pressure is so low that practically no collisions between molecules take place in the space between the moving surfaces. This is the case if the mean free path is large in comparison with the distance d between the surfaces. Then the $N_A/3V$ molecules per cc., which, according to the simplest argument are considered to have thermal velocities in the vertical direction, simply move back and forth between the plates and are the only ones to hit the plates at all. The $N_A/6V$ molecules moving downwards have, aside from their thermal velocity $|\overline{w}|$, an X-component of velocity equal to W_0 which they have received upon reflection from the upper plate, while the molecules moving upwards have no excess velocity since they were last reflected from the stationary lower plate. Therefore, the average velocity of the mass motion of the gas does not, as before, increase linearly with z, but is constant throughout the entire region between the surfaces and equal to $W_0/2$, since half the molecules (those moving down) have a velocity of flow W_0 and the other half (those moving up) have zero velocity of flow. At the upper plate there is a discontinuity in velocity equal to

$$W_0 - \frac{W_0}{2} = \frac{W_0}{2} \tag{263}$$

[1] Cf. also M. Trautz and W. Weizel, *Ann. Physik*, **78**, 305 (1925); M. Trautz and A. Narath, *ibid.*, **79**, 637 (1926).

[2] A. Kundt and E. Warburg, *Pogg. Ann.*, **155**, 337, 525 (1875); E. Warburg, *ibid.*, **159**, 399 (1876).

and at the bottom plate

$$0 - \frac{W}{2} = -\frac{W_0}{2}. \tag{264}$$

The momentum along the X-axis received by the lower plate per square centimeter is therefore

$$\frac{M}{6V}|\overline{w}|W_0 = \frac{M|\overline{w}|c}{6}W_0 = \frac{2}{3}\sqrt{\frac{M}{2\pi RT}}pW_0, \tag{265}$$

since the approaching molecules have a velocity W_0 before reflection and zero velocity afterwards. A more exact calculation[1] shows that the factor 2/3 must be replaced by unity. The force is now proportional to the density since the influence of the proportionality of the number of momentum carriers to the density is no longer compensated by a decrease in the distance from which they come, this distance being the constant distance between the plates.

This change of apparent viscosity with pressure has been used to measure very low pressures either by noting the damping of a vibrating quartz fiber[2] or the damping of oscillating plates.[3] Only in the latter case can the absolute viscosity be calculated. Furthermore, Knudsen[4] has used this relation for a determination of the molecular weight of very small amounts of gas. He suspends a glass sphere, 3.4 cm. in diameter, from a quartz fiber 18 cm. long and 25.2 μ in diameter. The sphere is surrounded with a closely fitting spherical shell. Torsional oscillations are started in the suspended sphere and the damping (due to the suspension, etc.) is measured in a vacuum. The gas to be investigated is admitted to the space between the sphere and the shell at such a low pressure that the mean free path is large in comparison with the distance from the sphere to the shell and the damping is again determined.

In the general case of moderate pressures it is to be expected that these same conditions as considered above will hold throughout a region adjacent to the moving surfaces and about one mean free path thick, since all the molecules coming up from the lower plate have zero velocity of flow and all those moving downwards have a flow velocity W' because they come from a layer Λ cm. away and W' is the velocity in that layer. (This is not exact due to the fact that the free paths are not all equal.) This velocity of flow W' in the next layer is larger, however, than the amount $\Lambda \frac{\partial W}{\partial z}$ which would at

[1] A. Timiriazeff, *Ann. Physik*, **40**, 971 (1913). (Taking into account the change in the distribution of velocity compared with the gas at rest.)

[2] I. Langmuir, *J. Am. Chem. Soc.*, **35**, 107 (1913); F. Haber and F. Kershbaum, *Z. Elektrochem.*, **20**, 296 (1914); A. Coolidge, *J. Am. Chem. Soc.*, **45**, 1637 (1923).

[3] I. Langmuir, *Phys. Rev.*, **1**, 337 (1913); S. Dushman, *ibid.*, **5**, 212 (1915); High Vacuum Technique; L. Dunoyer, Vacuum Practice (trans. by J. H. Smith, D. Van Nostrand Co. (1928)).

[4] M. Knudsen, *Ann. Physik*, **44**, 525 (1914).

first glance be expected. The reason for this is as follows: In unit time $\frac{N_A|\overline{w}|}{6V}$ molecules move downward and collide with 1 sq. cm. of the surface.[1] Each molecule brings to the surface an amount of momentum mW'. The molecules leaving the surface have, on the average, no excess momentum in the X-direction. Therefore the amount of momentum brought to unit area of the surface per second is $\frac{N_A|\overline{w}|}{6V} mW'$ and this must be equal to the flow of momentum in the interior of the gas;

$$\frac{N_A|\overline{w}|}{6V} mW' = \frac{N_A|\overline{w}|}{3V} \Lambda m \left(\frac{\partial W}{\partial z}\right)_{int} \tag{266}$$

or

$$W' = 2\Lambda \left(\frac{\partial W}{\partial z}\right)_{int} \tag{267}$$

There is, therefore, a more rapid decrease of velocity at the surface. Correspondingly, the velocity at a distance Λ from the upper surface is

$$W_0 - W' = W_0 - 2\Lambda \frac{\partial W}{\partial z}. \tag{268}$$

The discontinuity in velocity, that is, the difference between the average velocity of the gas at the bottom plate and the velocity of this plate is therefore

$$\tfrac{1}{2}(W' + 0) = \frac{W'}{2} = \Lambda \frac{\partial W}{\partial z}, \tag{269}$$

where the first summand corresponds to the molecules coming from above and the second to the reflected molecules. The slope of the velocity gradient within the gas and therewith the force on the plates is decreased by this slip. Within the gas, the velocity decreases from $W_0 - W'$ (near the upper plate) to W' over the distance $d - 2\Lambda$. Therefore

$$\frac{\partial W}{\partial z} = \frac{W_0 - 2W'}{d - 2\Lambda} = \frac{W_0 - 4\Lambda \dfrac{\partial W}{\partial z}}{d - 2\Lambda}, \tag{270}$$

whence [2]

$$\frac{\partial W}{\partial z} = \frac{W_0}{d + 2\Lambda}. \tag{271}$$

Thus the effect of the slip is equivalent to an increase of the distance between the plates by the amount 2Λ. The force then becomes

$$\frac{c|\overline{w}|M\Lambda}{3} \frac{W_0}{d + 2\Lambda} \tag{272}$$

[1] The more exact calculation of Timiriazeff gives 2/3 of this value.

[2] According to Timiriazeff, $4\Lambda/3$ is to be substituted for 2Λ.

instead of

$$\frac{c|\overline{w}|M\Lambda}{3}\frac{W_0}{d}.$$

Coefficient of Slip: These ideas have been generalized still further by Maxwell [1] and also by Knudsen and Smoluchowski through the assumption that a fraction of the molecules hitting the plate equal to $1-f$ is reflected elastically, the components of velocity in the plane of the plate remaining unchanged. Then only the fraction f of all the molecules assumes the velocity of the plate (W_0 or 0) upon reflection. These may be thought of as being "emitted" from the plate. Since only this fraction f transfers momentum to the plates, the equation for W' takes the form

$$f\frac{c|\overline{w}|}{6}MW' = \frac{c|\overline{w}|\Lambda M}{3}\frac{\partial W}{\partial z}. \tag{274}$$

Therefore W', the velocity of the gas at distance Λ from the bottom plate is given by

$$W' = 2\frac{1}{f}\Lambda\frac{\partial W}{\partial z}. \tag{275}$$

The decrease of velocity within the gas is then

$$\frac{\partial W}{\partial z} = \frac{W_0 - 2W'}{d - 2\Lambda} = \frac{W_0}{d + \dfrac{2-f}{f}2\Lambda} \tag{276}$$

and the force is

$$F = \frac{c|\overline{w}|M\Lambda}{3}\frac{W_0}{d + \dfrac{2-f}{f}2\Lambda} \tag{277}$$

$\dfrac{2-f}{f}2\Lambda$ is called the coefficient of slip. It is inversely proportional to the density and has the dimensions of a length.[2] The change in velocity at the boundary is

$$\tfrac{1}{2}\left[W' + (1-f)W' + f.0\right] = \frac{2-f}{2}W' = \frac{2-f}{f}\Lambda\frac{\partial W}{\partial z}. \tag{278}$$

Smoluchowski has shown that this same formula is obtained if it be assumed that the velocities of all the molecules after reflection are equal to W'', which is

[1] Clerk Maxwell, *Phil. Trans.*, **170**, 231 (1880).

[2] The formal hydrodynamic definition of external friction comes from the postulate that the force exerted on the plate by the external friction is equal to the flow of momentum in the interior of the fluid: Coefficient of external friction $\eta_e \times$ change in velocity at the boundary $= \eta(\partial w/\partial z)$. η/η_e is defined as the slippage coefficient. From (278) it follows that this is in agreement with the present usage.

between the velocity of the plate (0) and the initial molecular velocity (W')

$$W'' = (1 - f)W' + f.0. \tag{279}$$

To summarize, it may be pointed out that the first part of the discussion leading to equation (247) neglected the effect of slip. The next relation developed (equation (265)) refers to conditions at which there is maximum slip. Equation (273) applies to the pressure region between the two extremes. In other words, equation (247) takes account only of internal friction, equation (265) only of external and equation (273) of both, the coefficient of slip being 2Λ since $f = 1$. Finally, equation (277) shows the effect of both internal and external friction when the fraction f of the molecules colliding with the moving surface rebound without changing their tangential component of velocity.

Baule [1] has attempted to obtain a closer insight into the mechanism of the action between the plate and the gas molecule by assuming that the plate is itself made up of molecules which are bound elastically to one another in a regular lattice. He idealises the interaction by postulating that, upon collision with a solid, a gas molecule is either reflected, in which case it retains a fraction α of its original velocity of flow, or, if not reflected, the gas molecule is drawn into the interior of the lattice. When it comes out again it has taken up the velocity of the plate which, for example, is zero if it is the bottom plate. The transport of momentum then equals

$$(1 - f)(1 - \alpha)\frac{c|\overline{w}|}{6}MW' + f\frac{c|\overline{w}|}{6}MW' = \frac{c|\overline{w}|\Lambda}{3}M\frac{\partial W}{\partial z}, \tag{280}$$

where the quantity $f + (1 - f)(1 - \alpha)$ takes the place of f in the equations (275), (276), (277) and (278). The coefficient f is obtained from

$$1 - f = \frac{\pi}{2}(r + r^*)^2\frac{1}{a^2}\left(\frac{m^* - m}{2m^*} + ln\frac{2a}{r + r^*}\right), \tag{281}$$

where the starred symbols refer to the solid body of lattice constant a (cf. Chapter V). r and r^* are the molecular radii of the gas and the solid body. Further

$$\alpha = \frac{m}{m + m^*}. \tag{282}$$

Thus if m^*, the mass of the wall molecules is very small in comparison to m, the mass of the gas molecule, α approaches unity. If m is small, α is also small, and

$$f + (1 - f)(1 - \alpha) = 1 - \alpha(1 - f) \tag{283}$$

or almost unity. Baule's work is in good agreement with the experimental data obtained by Timiriazeff. It might be mentioned that Maxwell [2] had

[1] B. Baule, *Ann. Physik*, **44**, 145 (1914).

[2] Clerk Maxwell, *Phil. Trans.*, **170**, 231 (1880); *Scient. Papers*, **2**, 681, 705, Cambridge, 1890.

already hinted at ideas similar to the ones employed in the foregoing. Recent experiments by Ellett and Olson[1] have shown that cadmium and mercury atoms are reflected specularly from a clean rock salt surface but that sodium atoms are not reflected at all. Johnson[2] has found that hydrogen atoms are diffusely reflected from a number of crystal surfaces, provided that the temperature of the surface is high enough. Other results will come up later (p. 186).

The Flow of Gases through Small Orifices: Gas flow through orifices is also a case in which the behavior at very low pressures is quite different from that at normal pressures. The case of low pressures will be treated first because it is simpler.

Consider a vessel connected to an evacuated space through a small opening in a thin wall. Throughout this discussion a pressure will be considered low if the mean free path of the gas at that pressure is large in comparison with the dimensions of the orifice. Similarly a high pressure is one at which the mean free path is small in comparison with the dimensions of the orifice.

(*a*) *Very Small Pressures:*[3] If the orifice is small in comparison with the mean free path, a molecule upon hitting the opening will not, in general, collide with another molecule in the orifice but will continue to move in the direction of its original velocity. On the other hand, the distribution of the gas molecules inside the vessel in the neighborhood of the small hole is only slightly different from that prevailing at any other point near the wall. Consider, for example, that the opening is closed for an instant. Most of the molecules which move chaotically at a distance Λ (one free path) from the closed orifice come from the interior of the gas or have just been reflected from that part of the wall which does not constitute the opening. The fraction of these molecules which have been reflected from the covering of the hole, and which will be missing upon removal of the covering, is very small $\left(\sim \frac{\text{area of hole}}{2\pi\Lambda^2}\right)$. At the distance Λ from the opening, therefore, the presence of the opening does not greatly affect the distribution of the gas. Since, however, the molecules hitting the hole come from a distance Λ (if, as has been assumed, the opening in question is in a large plane wall) their number can be set equal to the number of molecules hitting an area of the original unperforated wall equal to the size of the opening, A. This number is equal to

$$N = \tfrac{1}{4}AN_Ac|\bar{w}| = \tfrac{1}{4}AN_Ac2\sqrt{\frac{2kT}{\pi m}} = \frac{AN_Ap}{\sqrt{2\pi MRT}}. \qquad (284)$$

Thus, the amount of gas flowing out through the orifice is proportional to the

[1] A. Ellett and H. F. Olson, *Phys. Rev.*, **31**, 643 (1928).

[2] T. H. Johnson, *J. Franklin Inst.*, **206**, 301 (1928).

[3] W. Thomson, Clerk Maxwell, *Phil. Trans.*, **170**, 231 (1880); *Scient. Papers*, **2**, 681, 711, Cambridge (1890).

area of the orifice, to the density, to the square root of the temperature and inversely proportional to the square root of the molecular weight. In a mixture of several gases each constituent flows through the opening as if the others were not present.

The molecules move into the evacuated space with velocities of the same magnitude and direction that they had upon passing through the orifice, that is to say, their velocities are distributed uniformly in all directions. The opening acts as if the molecules left it in the same manner that light leaves a glowing surface (Lambert's Cosine Law).[1] There is, therefore, no formation of a ray. If the region outside the containing vessel were not completely evacuated but contained a rarefied gas which might or might not be the same as the first, the amount of gas passing through the opening would be not affected by this fact and is therefore again given by equation (284). Since negligibly few collisions take place within the orifice a similar statement holds for the flow of gas in the reverse direction. Consider, for example, the case in which oxygen is the gas within the vessel and hydrogen at an equal pressure is outside. At the start of the flow, the pressure within the vessel increases because hydrogen, due to its sixteen times smaller molecular weight, comes in four times as fast as the oxygen leaves. On the other hand, the partial pressure of the oxygen is continually decreasing on the inside and increasing on the outside until equality is reached. Similarly, the partial pressure of the hydrogen on the inside increases and on the outside decreases until it also is equalized. Even if the initial pressure of the oxygen is twice as great as that of the hydrogen, a relatively larger amount of hydrogen will still flow in at the beginning so that the pressure difference increases. Of course work obtained from this process would not be in contradiction to the Second Law of Thermodynamics, since the pressure increase is merely due to the free energy decrease attending the irreversible expansion upon diffusion. Analogies to this will appear in other phenomena of flow through capillary tubes which, together with their applications, will be discussed below.

The relations deduced in this section have been employed by a number of investigators for various physical measurements. Knudsen[2] has shown that equation (284) can be used to determine either the molecular wieght of the flowing gas or its temperature. He has also applied the relation to the measurement of the vapor pressure of mercury. Other workers[3] have utilized the same general method to determine various other small vapor pressures. The experiment consists merely in determining the weight of material flowing in unit time at constant temperature through a small hole of known area. Since all the other quantities in equation (284) are known, the vapor pressure follows from a simple calculation.

[1] H. Mayer (*Z. Physik*, **52**, 235 (1928)) has given an experimental proof of this statement. He measured the number of molecules leaving a small hole by means of a torsion balance.

[2] M. Knudsen, *Ann. Physik*, **28**, 998 (1909); **29**, 179 (1909).

[3] A. C. Egerton, *Phil. Mag.*, **33**, 33 (1917); *Proc. Roy. Soc.*, **103A**, 469 (1923); Swan and Mack, *J. Am. Chem. Soc.*, **47**, 2112 (1925).

Weide and Bichowsky [1] have developed a method for the determination of the degree of dissociation of a gas at various temperatures by studying the effusion of the gas through a small hole. In their experiment, a small constant flow of the gas to be studied is established through the apparatus. The gas is led at a pressure of a few tenths of a millimeter of mercury to a furnace from which it escapes through a small hole to a highly evacuated space. The high pressure side of the small hole is connected to an accurate pressure measuring device. If the temperature of the furnace is raised, the gas in front of the small hole is partially dissociated according to the reaction

$$X_2 \rightleftharpoons 2X.$$

The pressure on the high pressure side of the small hole will have to be changed since the number of molecules passing through the small hole in unit time has to be increased in order to keep the total mass flowing unchanged. Thus, if there were no dissociation, the pressure would be p' given by the equation

$$N' = \frac{AN_A p'}{\sqrt{2\pi M_{X_2} RT}} \tag{285}$$

where N' is the number of molecules (X_2) entering the apparatus in unit time. If, however, the gas is dissociated, the atomic and molecular forms do not interfere with each other as to flow, so that

$$N_{X_2} = \frac{AN_A p_{X_2}}{\sqrt{2\pi M_{X_2} RT}} \tag{286}$$

and

$$N_X = \frac{AN_A p_X}{\sqrt{2\pi M_X RT}}, \tag{287}$$

where N_{X_2} is the number of molecules flowing out per second and N_X the number of atoms, p_{X_2} and p_X being the respective partial pressures. Since

$$N' = N_{X_2} + \tfrac{1}{2}N_X$$

and

$$p = p_{X_2} + p_X,$$

where p is the measured total pressure at the small hole, there may be obtained the relation

$$p_X = \frac{\sqrt{2}}{\sqrt{2} - 1}(p - p'). \tag{288}$$

Since p is measured directly and p' may be calculated, the partial pressure of the atomic form follows at once. DeVries and Rodebush [2] have used this method to determine the equilibrium constants for the dissociation of iodine

[1] H. Weide and F. R. Bichowsky, *J. Am. Chem. Soc.*, **48**, 2529 (1926).

[2] T. DeVries and W. Rodebush, *J. Am. Chem. Soc.*, **49**, 656 (1927).

and bromine. It has also been used by Bichowsky and Copeland [1] for the determination of the degree of dissociation of the hydrogen drawn from a discharge tube. This latter quantity has also been measured by Wrede.[2] Instead of measuring a steady flow, he investigated the pressure difference across a small hole through which there is no resulting transport of mass. A glass wall perforated by a small orifice separates two vessels, both of which are closed. In one of them the dissociation process takes place, Wrede using for this purpose an electric discharge rather than heat. The other vessel contains a catalyst placed before the orifice so that particles entering through the opening strike the catalyst immediately, atoms combining to form molecules. The resulting formula is again (288).

A further application of the flow through small orifices has been found in the production of rays of molecules. (See also p. 111 ff.) [3] These molecular beams are produced by permitting a gas to flow from a chamber with relatively high pressure but still within the limits stated on p. 164 through a small hole or slit into an evacuated space. The emergent molecules are distributed according to the Cosine Law (note 1, p. 165); hence there is as yet no ray formation. If a second slit is placed if front of the first, however, the two together define a beam of molecules. It is necessary, of course, that the spaces between the slits and through which the beam is expected to move be evacuated to such an extent that the mean free path of the molecules is large in comparison to the dimensions of the apparatus so that there will not be enough intermolecular collisions to destroy the definition of the beam. As the pressure on the high pressure side of the first slit is increased a point is finally reached when this condition is no longer fulfilled and from then on the definition of the the beam becomes worse and worse. The intensity of the beam may be calculated directly from equation (284). The optimum working conditions will be found in the articles referred to at the beginning of this paragraph.

(*b*) *Average and Higher Pressures*: If the dimensions of the orifice are large in comparison to the mean free path, the situation is quite different. The disturbance caused by the presence of the orifice is evident throughout the greater portion of the gas around the opening. The distribution of velocity within the vessel is changed so that there is a motion of the entire gas in the neighborhood toward the opening. The kinetic energy of the discharged gas is no longer distributed symmetrically between the three coordinate directions but there is a kinetic energy of the gas as a whole and hence a pronounced jet of gas leaves the orifice. Here the flow is determined by the total pressure difference across the orifice. Thus, to return to the previous illustration, if the oxygen pressure inside the vessel equals the hydrogen pressure outside, there is, on the whole, no flow of gas, because there is no difference in the *total* pressure on the two sides of the orifice. The partial pressures are equalized

[1] F. R. Bichowsky and L. C. Copeland, *J. Am. Chem. Soc.*, **50**, 1315 (1928).

[2] E. Wrede, *Z. Instrumentenk.*, **48**, 201 (1928); *Z. Physik*, **54**, 53 (1929).

[3] O. Stern, *Z. Physik*, **39**, 751 (1926); F. Knauer and O. Stern, *ibid.*, **39**, 764 (1926); T. Johnson, *Phys. Rev.*, **31**, 103 (1928).

by diffusion (p. 209). If the oxygen pressure inside is greater than the hydrogen pressure outside, the oxygen flows out on account of the difference in total pressures, and the inward diffusion of the hydrogen does not begin until the total pressures have become equal or at least nearly so. (For the effect of temperature differences, cf. p. 215.)

Further problems arising in this connection have not been investigated from the point of view of the theory of gases (e.g., with regard to the distribution of velocities). Rather must they be attacked with the methods of hydrodynamics. The theory of gases is applicable only in so far as it is capable of leading to the deduction of the hydrodynamic or aerodynamic equations, including their supplementary terms.[1]

Bunsen [2] has determined the molecular weights of gases by allowing the gas to stream out of a hole 1/10 to 1/100 mm. diameter and setting the volume passed in unit time proportional to $1/\sqrt{M}$. This procedure, however, is not founded on the kinetic theory directly, but on hydrodynamics, since it determines primarily the density of the gas. The kinetic energy of the flow, is determined principally by the pressure difference; it also depends on C_p/C_v and must be corrected for friction. The pressure difference being kept the same, the kinetic energy $\frac{1}{2}\rho w^2$ will be the same and therefore the velocity inversely proportional to the square root of the density. But, from the gas laws, the density is proportional to M, hence the volume passed in unit time is inversely proportional to the square root of the molecular weight.

Further information regarding the carrying out of these measurements and the results obtained from them may be found in the standard texts on hydrodynamics.

Flow through Tubes: Consider now the case in which the two vessels are connected by means of a tube instead of an orifice. The tube is to be straight and of circular cross section with diameter d.

(*a*) *Mean Free Path Large in Comparison to d*: The flow of gas under this condition has been named by Knudsen " Molecular Flow." If the gas molecules were reflected elastically from the wall of the tube (which is supposed smooth), the flow through the tube would be identical with the previously discussed case of the flow through an orifice in a plane, thin wall. All the molecules entering the mouth of the tube would pass through into the second vessel. That is, the quantity of gas flowing through the tube in unit time would be independent of the length of the tube and equal to the amount of gas passed by an orifice of equal size under the same conditions of pressure, etc. Moreover, the directions of the velocities of the molecules would be distributed as in the previous case. Since, however, the amount of gas passed is found to depend on the length of the tube, the assumption of elastic reflections from the tube wall cannot be correct. To take the place of this assumption, Knudsen

[1] M. Knudsen, *Ann. Physik*, **28**, 75 (1909); **35**, 389 (1911); M. v. Smoluchowski, *ibid.*, **33**, 1559 (1910). Cf. also O. Reynolds, *Phil. Trans.*, **170**, 727 (1880); Papers, I, 257, Cambridge (1900).

[2] R. Bunsen, Gasometr. Methoden, Braunschweig (1857). Cf. also H. Eyring, *J. Am. Chem. Soc.*, **50**, 2398 (1928).

has postulated that " emission " takes place from the wall of the tube instead of reflection. By this it is meant that the molecules leave a surface uniformly in all directions regardless of the directional distribution with which they hit the surface. As a result of this behavior some of the entering molecules are reversed and sent back to the vessel from which they came. The longer the tube, the greater the fraction of molecules thus returned. Hence the amount of gas flowing through the tube must diminish with increasing length of the tube. According to this hypothesis, the number of molecules entering the tube but which are turned back within it, returning to the vessel from which they came, is a certain fraction of the total number of entering molecules. This fraction is determined only by the number of collisions with the wall of the tube and not by collisions between molecules. It is therefore independent of the concentration of the gas, the molecular diameter and the presence of another gas (provided that the mean free path of the other gas is also large in comparison with the diameter of the tube.)

If $\mathbf{N}$ is the number of molecules hitting unit area in unit time, the excess flow of molecules from left to right (along the positive X-axis) is found to be

$$\frac{1}{2} B \frac{d\mathbf{N}}{dx}, \tag{289}$$

where for circular tubes

$$B = \frac{2d^3\pi}{3}.^{1} \tag{290}$$

[1] The deduction proceeds thus:

The number of molecules hitting a certain part of the wall will first be investigated in respect to the point from which they come. An element dA' of the tube wall sends out a cone of molecules (Fig. 24). The solid angle of the cone is $d\omega' = \sin \varphi' d\varphi' d\epsilon'$ where φ' is the angle between the axis of the cone and the normal to the surface and ϵ' an angle measured in the plane of dA' from an arbitrary line in this plane, corresponding to the geographical longitude. (φ' and ϵ' are the angles of a set of space polar coordinates with axis normal to dA'.) The number of molecules sent out into this cone from the element dA' in unit time is

$$\mathbf{N}' \frac{d\omega'}{\pi} \cos \varphi' dA' \tag{291}$$

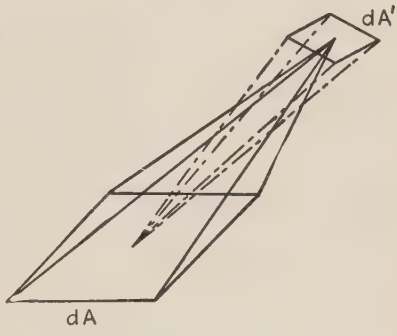

Fig 24.

because the quantity $\cos \varphi' \, dA'$ is the projection of the surface dA' on a plane perpendicular to the axis of the cone (the name Cosine Law being due to the factor $\cos \varphi'$). This solid angle $d\omega'$ is completely filled by another elementary surface dA at a distance r from dA' if

$$d\omega' = \frac{dA \cos \varphi}{r^2}, \tag{292}$$

where φ is the angle between the normal to dA and the axis of the cone. (The numerator of this expression is, as before, the projection of dA perpendicular to the axis of the cone). The

Since the quantity $\mathbf{N}$ decreases linearly with x, and since its value at the inlet to the tube is

$$\frac{N_A c_2 |\overline{w}_2|}{4} = N_A \frac{p_2}{\sqrt{2\pi MRT_2}}, \tag{302}$$

and at the outlet is

$$\frac{N_A c_1 |\overline{w}_1|}{4} = N_A \frac{p_1}{\sqrt{2\pi MRT_1}}, \tag{303}$$

the number of mols of gas flowing through the tube per second is given by

$$\frac{dn}{dt} = \tfrac{1}{2} B \frac{1}{\sqrt{2\pi MR}} \left(\frac{p_2}{\sqrt{T_2}} - \frac{p_1}{\sqrt{T_1}} \right) \frac{1}{L}, \tag{304}$$

where L is the length of the tube.

number of molecules crossing the surface dA and coming from the direction of dA' is then

$$\frac{\mathbf{N}' \cos \varphi' \cos \varphi}{\pi r^2} dA dA', \tag{293}$$

But the total number of molecules crossing this surface dA coming from all possible directions (from all the elements of area dA') is

$$\frac{dA}{\pi} \int \frac{\mathbf{N}' \cos \varphi \cos \varphi'}{r^2} dA' \tag{294}$$

or

$$\frac{dA}{\pi} \int \mathbf{N}' \cos \varphi \sin \varphi \, d\varphi \, d\epsilon \tag{295}$$

since

$$d\omega = \sin \varphi \, d\varphi \, d\epsilon = \frac{dA' \cos \varphi'}{r^2} \tag{296}$$

is the solid angle which originates at dA and is subtended by dA'.

The relation between the number $\mathbf{N}'$ and the distance along the tube must now be determined. To effect this the area dA is chosen as a portion of the tube wall itself at the point x_0. The number of molecules, $\mathbf{N}(x_0)dA$, leaving this point must be equal to the number coming to it:

$$\mathbf{N}(x_0)dA = \frac{dA}{\pi} \int \mathbf{N}(x') \sin \varphi \cos \varphi \, d\varphi \, d\epsilon. \tag{297}$$

$\mathbf{N}(x')$ may be developed into the series

$$\mathbf{N}(x') = \mathbf{N}(x_0) + (x' - x_0) \frac{d\mathbf{N}}{dx} + \frac{(x' - x_0)^2}{2} \frac{d^2\mathbf{N}}{dx^2} + \cdots. \tag{298}$$

There is then obtained

$$\mathbf{N}(x_0) = \frac{\mathbf{N}(x_0)}{\pi} \int \sin \varphi \cos \varphi d\varphi d\epsilon + \frac{1}{\pi} \left(\frac{d\mathbf{N}}{dx} \right)_{x=x_0} \int (x' - x_0) \sin \varphi \cos \varphi d\varphi d\epsilon + \frac{1}{\pi} \frac{d^2\mathbf{N}}{dx^2} \int \frac{(x' - x_0)^2}{2} \sin \varphi \cos \varphi d\varphi d\epsilon + \cdots. \tag{299}$$

The first integral on the right equals π and the second vanishes, since for each positive value of $x' - x_0$ there is an equal negative value. Hence the equation reduces to

$$\mathbf{N}(x_0) = \mathbf{N}(x_0) + \frac{1}{\pi} \left(\frac{d^2\mathbf{N}}{dx^2} \right)_{x=x_0} \int \frac{(x' - x_0)^2}{2} \sin \varphi \cos \varphi d\varphi d\epsilon + \cdots. \tag{300}$$

For the case of constant temperature this becomes [1]

$$\frac{dn}{dt} = \frac{1}{2}\frac{B}{\sqrt{2\pi MRT}}\frac{1}{L}(p_2 - p_1) = \frac{1}{2}\frac{B}{\sqrt{2\pi M}}\frac{\sqrt{RT}}{L}(c_2 - c_1). \tag{306}$$

This equation is formally the same as the one obtained for small orifices $A\sqrt{\frac{RT}{2\pi M}}(c_2 - c_1)$ with the exception that in the place of A there appears

From this it follows that the second and higher differential quotients must vanish and $\mathbf{N}$ therefore is a linear function of x.

In order to calculate the number of molecules passing through the tube the surface dA is now chosen to be an element of the cross section. If the tube has a circular cross section of diameter d, the excess of molecules passing from left to right through dA, which is placed at x_0 and is a distance r from the center of the tube is

$$\begin{aligned} dA\Bigg\{&\left[\mathbf{N}(x_0) + \frac{1}{\pi}\frac{d\mathbf{N}}{dx}\int_0^{\pi/2}\int_0^{2\pi}(x - x_0)\sin\varphi\cos\varphi d\varphi d\epsilon\right] \\ &- \left[\mathbf{N}(x_0) - \frac{1}{\pi}\frac{d\mathbf{N}}{dx}\int_0^{\pi/2}\int_0^{2\pi}(x - x_0)\sin\varphi\cos\varphi d\varphi d\epsilon\right]\Bigg\} \\ &= 2\frac{dA}{\pi}\frac{d\mathbf{N}}{dx}\int_0^{\pi/2}\int_0^{2\pi}(x - x_0)\sin\varphi\cos\varphi d\varphi d\epsilon. \end{aligned} \tag{301}$$

In this position of dA, the axis from which φ is measured is parallel to the axis of the tube, while before it was normal to it. The difference between the number of molecules coming from the right and from the left is now taken rather than, as in the previous case, the sum. Let the distance from dA to the periphery of the cross section of the tube be ρ. Then

$$x - x_0 = \rho\cot\varphi$$

and, upon introducing the central angle, ϑ, there is obtained from (301)

$$\frac{1}{2}\frac{d\mathbf{N}}{dx}\cdot dA\frac{d}{2}\int_0^{2\pi}\frac{\frac{d}{2} + r\cos\vartheta}{\sqrt{\frac{d^2}{4} + r^2 + rd\cos\vartheta}}d\vartheta. \tag{301'}$$

The greatest flow prevails at the center ($r = 0$). Upon integrating over $dA = 2\pi rdr$ there is obtained the value of B given above. For square cross sections this quantity is $2.973\,l^3$. For rectangles, see Smoluchowski (loc. cit.).

[1] If only the fraction f of the molecules colliding with the wall is emitted, the remainder, $1 - f$, being reflected, the $\mathbf{N}f$ emitted molecules introduce the factor f into equation (306). The $1 - f$ molecules coming from the left which were reflected at the point $x_0 + (x' - x_0)$ have come there from the point $x_0 + 2(x - x_0)$ (Fig. 25). Of these molecules the fraction f had been emitted from the point $x_0 + 2(x' - x_0)$ and the reflected fraction, $1 - f$, had come from a point still farther to the left. The $f(1-f)\mathbf{N}(x_0)$ molecules which are emitted at the point $x_0 + 2(x' - x_0)$ and which are then reflected unchanged from the point $x_0 + (x' - x_0)$ add to the flow twice as much as would the same number of molecules emitted at the point x' because they come twice as far. Furthermore, there are missing from the molecules which pass the point x_0 to the left, coming from the right, those which have not been emitted to the left at the point $x_0 - (x' - x_0)$ but which were reflected to the right at this

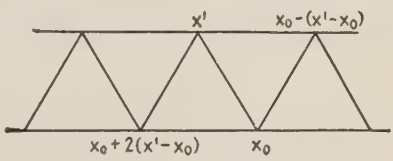

FIG. 25.

the quantity

$$\frac{B}{2L} = \text{cross section}\,\frac{4d}{3L}$$

(for cylindrical tubes).[1]

In the case of non-cylindrical tubes, provided that the dimensions are so small that there are only collisions with the wall and negligibly few between molecules, there is to be expected a formula of the type

$$\frac{B'}{\sqrt{MRT}}(p_2 - p_1), \tag{307}$$

where B' has the dimensions of an area and depends only on the dimensions and shape of the tube and not on the gas. Thus, in all these cases, the amount of gas flowing per unit time will be directly proportional to the pressure difference and inversely proportional to the square root of the temperature (or directly proportional to the difference in concentration and the square root of the temperature) and inversely proportional to the square root of the molecular weight. Graham [2] discovered these results long before the development of the kinetic theory in the course of his experiments upon the passage of gases through porous plates such as gypsum and meerschaum, the pores of such materials being small in comparison to the mean free path. He called this effect the transfusion or effusion of gases. His results have been checked by other workers.

The point must be emphasized here that in the motion of a mixture of gases, each constituent is completely independent of the others, as is the case with small orifices, since the molecules do not affect each other within the tube and since their motion is entirely determined by the character of the wall of the tube. Consider two vessels, A and B, which are separated only by a porous plate. Let A contain hydrogen at one atmosphere pressure, and B oxygen at two atmospheres. Then at the outset the partial pressure of hydrogen in A is 1 and in B, 0; the partial pressure of oxygen in A is 0 and in B is 2. The hydrogen will effuse from A to B and the oxygen from B to A without inter-

point. This portion, $f(1-f)B(d\mathbf{N}/dx)dA$, which is missing from the reverse current, also increases the excess flow to the right so that those molecules which are reflected *once* contribute to the flow an amount equal to $3f(1-f)(d\mathbf{N}/dx)B$. Correspondingly, the contribution from those which are reflected twice in succession is equal to $(3+2)f(1-f)^2(d\mathbf{N}/dx)B$. On summing, the factor to be applied to (306) is

$$f[1 + 3(1-f) + 5(1-f)^2 + \ldots] = \frac{2-f}{f}. \tag{305}$$

This formula is only valid as long as f is sufficiently large or the tube sufficiently long to ensure that each molecule is emitted at least once.

[1] Cf. also P. Clausing, *Verslag Akad. Wetesch. Amsterdam*, **35**, 1023 (1926).

[2] T. Graham, *Quart. Journ. of Science*, **2**, 74 (1829); *Phil. Mag.*, (3) **2**, 175, 269, 351 (1833); *Pogg. Ann.*, **17**, 341 (1829); **28**, 331 (1833); **120**, 415 (1863); *Phil. Trans.*, (1863) *p.* **385**; G. Hüfner, *Wied. Ann.*, **16**, 260 (1882); E. Reusch, *Pogg. Ann.*, **124**, 434 (1865). Bunsen's anomalous results, according to Graham, are to be attributed to too large openings (R. Bunsen, Gasometr. Methoden, Braunschwieg, 1857).

fering with each other within the plate. If the partial pressures in the two containers are so small that the mean free path is large in comparison to the dimensions of the containers, the entering gas is distributed throughout the entire compartment. Otherwise the gas must be stirred in order that the partial pressures of the gases at the plate may not be more (or less) than the average partial pressure of the corresponding gas throughout the bulk of the container. Now, since the molecular weight of hydrogen is only one sixteenth of that of oxygen, the hydrogen passes through the plate four times as rapidly as oxygen at the same pressure. Thus, although the initial pressure of the oxygen is twice as great as that of the hydrogen, the latter passes through the plate twice as fast as the former. Thus, at the outset, twice as much hydrogen enters B as oxygen leaves B. Hence, the total pressure in B increases at the beginning of the process, in spite of the fact that it was already twice as great as the pressure in A. The effusion of hydrogen ceases when its partial pressure in A equals its partial pressure in B. The equalization of the oxygen pressures proceeds more slowly.

For purposes of comparison, consider the case in which the connecting tube is of relatively large diameter. The direction of the flow is then determined, not by the partial pressures, but by the total pressure. Therefore, in the foregoing illustration, the oxygen flows at once into the hydrogen compartment until the total pressures in the two vessels are equal. Only thereafter does the much slower equalization of the partial pressures caused by the partial pressure gradient become evident, although, of course, this diffusion also sets in at the first instant (cf. p. 209). If the total pressures in the two compartments are initially equal there is no streaming of the gas at the outset the only process taking place being diffusion.

The dependence of the velocity of effusion upon molecular weight has been used to detect fire damp in mines. For this purpose a closed porous vessel (e.g. gypsum) filled with air is attached to a pressure measuring device which can actuate an alarm. If fire damp (CH_4, $M = 16$) is present in the external air ($M \sim 29$) the pressure within the porous container increases and causes the alarm to sound. The velocity of effusion may also be used for the determination of molecular weight of gases (atmolysis). Conversely, mixtures of gases of different molecular weights can be fractionally separated by effusion.[1]

To return again to the case of the small tube of circular cross section some numerical examples will ge given. It must be remembered that the mean free path in hydrogen at a pressure of 0.1 mm. Hg equals about 1 mm. Suppose a space, in which a constant pressure of hydrogen equal to 0.1 mm. is maintained, be connected through a tube 1 mm. in diameter and 5 cm. long to a completely evacuated chamber. According to equation (304) 40 cc. of the gas at 0.1 mm. ($24. \times 10^{-8}$ mol) flow through the tube per second, a quantity which can be removed by good pumps. This is of fundamental importance in the investigation of canal rays which can only be produced in a space filled with

[1] F. Fischer, H. Schrader and A. Jager, *Brennstoff-Chem.*, **4**, 289 (1923); R. Lorentz and A. Magnus, *Z. anorg. allgem. Chem.*, **136**, 97 (1924).

gas, but which must be studied either in a high vacuum or in a different gas. Wien,[1] who developed this method, connected the space in which the canal rays are produced to the investigation chamber through a tube 2 mm. in diameter. The canal rays passed through this tube parallel to its axis. M. Knudsen has investigated the flow through still smaller tubes. For example, he connected two flasks of $2\frac{3}{4}$ liters contents by means of a tube 30 cm. long and 0.1 mm. in diameter. One flask was filled with hydrogen at about 0.01 mm. and the other was evacuated to as low a pressure as possible. It required about fifteen hours for $\frac{1}{3}$ of the gas to pass from the one flask to the other. The agreement with the formula (306) is satisfactory. Furthermore, according to (306) the time is independent of the total pressure if the latter is sufficiently small.

(*b*) *Poiseuille Flow*: This type of flow takes place through tubes whose diameters are large in comparison with the mean free path, but which are still small enough to be regarded as capillary tubes, which means that the viscosity is still an important factor. For small rates of flow the motion is determined by Poiseuille's Law, which states that the volume of fluid passing through the tube in unit time is

$$\frac{d^4\pi}{128}\frac{p_2 - p_1}{\eta L},$$

where L is the length of the tube. The deduction of this equation may be found in any standard text on hydrodynamics.[2]

The equation giving the flow in mols per second may also be written

$$\frac{d^2\pi}{12}\frac{3d^2}{32\Lambda}|\overline{w}|\frac{\partial c}{\partial x}. \tag{309}$$

If there were present no unsymmetrical velocity of flow (no deviation from Maxwell's Law) a deduction of the type employed on p. 153 would give the equation

$$\frac{d^2\pi}{12}|w|\Lambda\frac{\partial c}{\partial x}. \tag{310}$$

Actually, however, the flow is greater by the amount $3d^2/32\Lambda^2$.

The main difficulty encountered in applying this equation to the flow of gases is that it is valid as it stands for an incompressible fluid but, in the case of a gas, the specific volume changes along the tube with the pressure. Furthermore, a change in temperature is in general connected with the change in volume and the extent of this temperature change depends on the circumstances (properties of the tube wall). Under different conditions the expansion may be isothermal or adiabatic.

[1] W. Wien, *Ann. Physik*, **30**, 349 (1909).

[2] See M. Brillouin, Leçons sur la viscosité. Paris, 1907.

For a short interval of the tube the flow in mols may be written

$$\frac{dn}{dt} = \frac{d^4\pi}{128L} \int \frac{1}{\eta RT}\, pdp. \tag{311}$$

For an isothermal process with the limitation that η = constant [1] this gives the expression

$$\frac{dn}{dt} = \frac{d^4\pi}{128L\eta} \frac{1}{RT} \frac{p_2^2 - p_1^2}{2}. \tag{312}$$

The case of a polytropic expansion (i.e., one intermediate between an isothermal and adiabatic) (cf. Chap. II) has been treated by Fisher and by Holm.[2] For a given pressure difference $(p_2 - p_1)$ and temperature, as has been tested experimentally by Graham and Bunsen,[3] the flow (in grams) is proportional to $\left(\frac{p_1 + p_2}{RT}\right) M$, that is, to the average density of the gas. Increase in temperature decreases the amount of gas passed in unit time. The rate of flow can be used as a means of determining η. This has been done by O. E. Meyer, among others, and, more recently, by Rankine. The experimental details may be found in Brillouin's book. Two further corrections, however, must be applied to the formula before it can be used.

In order to derive the complete equation it must be pointed out first that only part of the pressure difference is utilized in overcoming friction, the remainder being required for the production of the kinetic energy of the mass motion. This latter portion, which was first considered by Hagenbach [4] and later by Brillouin (*loc. cit.*) and Smoluchowski [5] must be subtracted from the pressure difference. (Cf. equation (313)).

In the second place the gas does not stick to the walls of the tube, as has already been noted on p. 159 and as was first demonstrated experimentally by Warburg.[6] A finite slip with slippage coefficient $\frac{\eta}{\eta_e}\left(\frac{\eta}{\eta_e}\frac{\partial W}{\partial r} = \text{discontinuity in velocity at the boundary of the flowing gas}\right)$ requires the insertion of the factor $\left(1 + \frac{8\eta}{\eta_e d}\right)$ in equation (310). It has already been shown that η/η_e is directly proportional to the mean free path and is therefore inversely proportional to the pressure. The formula giving the number of mols flowing per second is then [7]

[1] O. E. Meyer, *Pogg. Ann.*, **127**, 253, 353 (1866).

[2] J. Fisher, *Phys. Rev.*, **29**, 149 (1909); R. Holm, *Ann. Physik*, **44**, 81 (1914); **45**, 1165 (1914).

[3] T. Graham, *Phil. Trans.*, **139**, 339 (1849); R. Bunsen, *loc. cit.*

[4] E. Hagenbach, Pogg. Ann., **109**, 835 (1860).

[5] M. v. Smoluchowski, *Bull. Acad. Krakau*, **143** (1903).

[6] E. Warburg, *Pogg. Ann.*, **59**, 399 (1876).

[7] Maxwell obtained this formula, except for the term correcting for the kinetic energy, from the theory of gases (*loc. cit.*, p. 709). Reynolds (*loc. cit.*, p. 351) has also arrived at an expression of similar character.

$$\frac{dn}{dt} = \frac{1}{8\eta L}\left(1 + \frac{8\eta}{\eta_e d}\right)\left[\frac{\pi d^4}{16RT}\frac{(p_2^2 - p_1^2)}{2} - \frac{M}{\pi}\left(\frac{dn}{dt}\right)^2\right], \qquad (313)$$

where the last term, which takes into account the kinetic energy, is only a correction term. At very small pressures the term $8\eta/\eta_e d$, corresponding to the slip, predominates and the equation reduces to (306) with, however, a different numerical factor. This means that the numerical factor of η_e depends upon the pressure in some way which is still unknown.

If the pressure difference is held constant and the correction for kinetic energy neglected, the quantity of gas flowing decreases with decrease in pressure due to the increase of the mean free path. Hence the amount of mols passed per second is proportional to $\frac{\alpha}{\Lambda} + \beta$. However, as soon as the motion is no longer determined by collisions between molecules but by collisions with the wall the quantity of gas passing is independent of the pressure.[1] If the flow of gas is expressed in terms of the volume or fractions of the amount of gas present in a vessel, the flow *increases* with decrease in pressure up to a certain value, after which it remains constant. The fact that upon evacuating a system the volumes removed decreases as the pressure falls, is explained by continuous decrease in the *pressure difference* upon which the flow depends.

Knudsen has shown equation (313) to be valid in the pressure interval of from 15 to 10^{-4} mm. of mercury, for hydrogen, oxygen and carbon dioxide. His results can be expressed satisfactorily if the numerical factor in the equation for the low pressure flow through tubes be multiplied by $\frac{1 + c_1 p}{1 + c_2 p}$, where c_1 and c_2 are constants.

This term is necessary for the expression of the experimental results because as the pressure is decreased the number of mols passed in unit time goes through a minimum before it attains its constant value. Knudsen has not taken into account that the numerical factor of slip depends upon the pressure, as pointed out above, because he assumes the approximate calculation, employed in the preceding discussion to be exact, and attempts to explain the minimum in another manner. Gaede [2] has further tested his results by allowing hydrogen at extremely low pressures to flow between two plates close together. He found that the formula (306) is followed exactly at pressures less than 0.001 mm. At higher pressures the minimum reappeared. Gaede showed that it is not caused by contaminating vapors.

(*c*) *Other Shapes*: The flow between two plates a small distance d apart is given by the expression

$$\text{Mols passing 1 cm. width per second} = \frac{d^3}{12\eta}\frac{1}{RT}\frac{p_2^2 - p_1^2}{2}. \qquad (314)$$

[1] This transition from Poiseuille flow to transfusion has also been investigated by C. Christiansen (*Ann. Physik*, **5**, 436 (1901)). It has been mentioned above that Graham had already explained the anomalous results of Bunsen by calling attention to the latter's use of too large openings.

[2] W. Gaede, *Ann. Physik*, **41**, 289 (1913).

Reynolds has deduced a similar formula from the theory of gases. If the plates are very close together, d being of the order of 10^{-4} cm., the amount of air at atmospheric pressure flowing through a width of 1 cm. under a pressure gradient of 1 mm. Hg/cm. equals 0.6×10^{-6} cc./sec. Stefan [1] has concluded from this that the difficulty attending the separation of two smooth plates which are in close contact, depends less upon the presence of attractive forces (adhesion) than upon the slow entry of the air through the narrow slit. The method of Fabry and Perot [2] for the determination of viscosity depends on the converse phenomenon, namely, the slow outflow of the gas from between two approaching plates. Two plates with known opposite electric charges are allowed to come together under their electrical attraction. The velocity of approach is measured optically by means of an interferometer and from this is calculated the velocity of efflux of the air. Precise measurements, as has already been noted, have been carried out at extremely low pressures by Gaede.[3]

(*d*) *Wide Tubes*: The Poiseuille formula holds only up to a certain velocity. This velocity is connected with the other conditions of the experiment by the "Reynold's number," [4]

$$[R] = \frac{rW\rho}{\eta}, \tag{315}$$

where r is the hydraulic radius of the tube,

$$r = \frac{\text{cross section}}{\text{periphery}}$$

For circular tubes $r = D/4$ where D is the tube diameter. If [5]

$$R > 580,$$

the streamline flow described by the Poiseuille formula ceases and turbulent flow sets in. The hydrodynamics of the latter case is at present being developed with great rapidity. It seems [6] that in rather long tubes, where the influence of the orifice (end effect) can be neglected, it is possible to write

$$-\frac{dp}{dx} = \beta \frac{\rho W^2}{2r}, \tag{316}$$

where β depends on the surface of the tube. For smooth tubes of glass,

[1] J. Stefan, *Wien. Ber.*, **69**, 713 (1874).
[2] C. Fabry and Perot, *Ann. Chim.*, **13**, 275 (1898).
[3] W. Gaede, *Ann. Physik*, **41**, 337 (1915).
[4] O. Reynolds, *Phil. Trans.*, **174**, 935 (1883).
[5] For circular tubes 4[R] is frequently called the Reynold's number.
[6] I. Ackerel, Handbuch der Physik, vol. VII, p. 304, Berlin (1927); A. Stodola and L, Lowenstein, Steam and Gas Turbines, vol. I, pp. 55–67, New York, (1927); A. B. Eason. Flow and Measurement of Air and Gases, London (1919); W. Kent, Mechanical Engineers Pocket Book, 10th Ed., p. 904, New York.

wrought metal, etc., the following formula is found to hold:[1]

$$\beta = 0.056 \frac{1}{\sqrt[4]{[R]}} \cdot \tag{317}$$

β is higher and follows a different rule for rough (rusty or muddy) pipes. Sometimes β may be taken as a constant.

If it be assumed that the heat conduction is sufficiently rapid to guarantee constant temperature throughout, equation (316) can be integrated. The result is for a tube of length L

$$L = \frac{2r}{\beta}\left\{ ln \frac{W_0}{W} + \frac{1}{2}\frac{p_0}{\rho_0}\left(\frac{1}{W_0^2} - \frac{1}{W^2}\right)\right\}, \tag{318}$$

with $\rho_0 W_0 = \rho W$ and $p_0 W_0 = pW$.

If the volume v is desired instead of the velocity W,

$$v = \frac{\pi}{4} d^2 W \tag{319}$$

and

$$v = \frac{\pi}{4}\sqrt{\frac{D}{2\beta\rho}\left(\frac{dp}{dx}\right)} \cdot \tag{320}$$

Stodola (*loc. cit.*) gives formulae for the case of adiabatic flow.

The Theory of the Molecular Pump: The fact that at very low pressures the flow through small openings is negligibly small has found an important technical application, aside from that in the investigations on canal rays, in the Gaede[2] molecular pump which depends upon an application of the considerations of p. 164. Consider a horizontal channel of height small in comparison to the mean free path. The lower limiting surface is moved to the right in a horizontal direction with the velocity W_0. All the molecules colliding with the bottom plate acquire an excess horizontal component of velocity equal to W_0. If the channel is closed at each end, there is developed a pressure difference between the left and the right ends which, at the steady state, amounts to

$$\frac{B}{2}\frac{dp}{dx}\frac{1}{\sqrt{2\pi MRT}} = N_A c A \frac{W_0}{2} \cdot \tag{321}$$

The left hand side of this expression gives the amount of gas flowing down the pressure gradient to the left, B being the constant of p. 169 which is dependent on the dimensions of the channel. The right hand side of the equation denotes the amount of gas piled up on the right through the cross section of the channel A, as a result of the mean velocity $W_0/2$ received from the moving plate. If the channel is closed at each end, but the ends provided with wide inlet and outlet tubes, there will be a suction at the left and an expulsion of

[1] H. Blasins, *Forschungsarb. Ver. D. Ing.*, **131** (1913).

[2] W. Gaede, *Ann. Physik*, **41**, 337 (1913).

gas at the right provided that the pressure has first been reduced so far that the mean free path is large in comparison with the dimensions of the channel. In practice the space between two cylinders takes the place of the channel, the inner cylinder being rapidly rotated. A metal vane extends from the outer stationary cylinder nearly to the inner moving one. The gas between the cylinders is swept away from one side of the vane to the other side. Tubes are sealed to the outer cylinder on both sides of the vane, one serving as inlet and the other as outlet. As was observed at the beginning of this paragraph the space between the rotating cylinder and the vane need not be tightly packed if this space is small in comparison with the cross section of the channel.[1]

The Gaede Kinetic Heat Effect: While investigating his molecular pump, Gaede [2] was led to the discovery of a new effect. Since the action of the molecular pump increases the velocities of the molecules along one direction and decreases their velocities in the opposite direction, an object placed in the moving gas will experience a rise in temperature on the side toward which the molecules are hurled by the rotor and a corresponding decrease on the opposite side. Gaede placed two thin copper plates in the moving gas at right angles to the direction of motion and found, as he had predicted, that the forward plate was warmed and the other cooled. The observed temperature rise was of the expected order of magnitude. The theoretical treatment of the effect has been extended by Weber [3] who showed that the temperature change depends on the accommodation coefficient of the particular gas used. Rucker [4] has employed Weber's equations to calculate a number of accommodation coefficients from measurements of the Gaede effect.

The Motion of Foreign Particles under the Influence of a Constant Force: [5] (*a*) *Small Particles:* [6] The motion of small foreign particles under a constant force through a gas is of great importance in many branches of physics. For example, in the conduction of electricity through gases the ions are impelled through the gas by the electric field. If these ions were in a vacuum and were acted upon by the constant force F, they would experience a constant acceleration $a_x = F_x/m$ and their velocities would increase continually,

$$W_x = a_x t = \sqrt{2a_x x}.$$

In a gas, however, they collide with the gas molecules, and it has already been proven that such collisions result in an equalization of the kinetic energy of the colliding bodies. On the average, therefore, upon colliding with the gas

[1] A pump utilizing the same principles as the foregoing, but embodying a number of mechanical improvements, has been designed by Holweck. Cf. L. Dunoyer, Vacuum Practice, page 36.

[2] W. Gaede, *ibid.*, p. 369.

[3] S. Weber, *Z. Physik*, **24**, 267 (1924).

[4] K. Rucker, *Ann. Physik*, **85**, 831 (1928).

[5] Throughout the following pages (179–209) w is used instead of $|w|$, for the magnitude of the velocity.

[6] We follow closely the comprehensive report of H. F. Mayer, *Jahrb. Radioakt. und Elektronik*, **18**, 201 (1921).

molecules the ions give up at least a part of the kinetic energy which they have obtained from the field of force and which is in excess of their normal thermal energy. The stationary state is reached when the mean energy loss of the ions per collision just equals the amount of energy they have gained since their last collision. The kinetic energy taken up by the gas molecules naturally increases their own kinetic energy and therefore the temperature of the gas. In this manner the frictional or resistance heat appears. This must be conducted away from the system if the process is to remain isothermal. In the following discussion the primed symbols will refer to the gas molecules and the unprimed to the foreign particles, in the present example, the ions. w_ϑ will be used to indicate the mean thermal velocity. $\left(w_\vartheta = 2\sqrt{\frac{2kT}{m\pi}} \cdot \right)$

The formulae applicable to this case were first deduced by Riecke and later by Drude [1] with the aid of the assumption that each ion loses its excess kinetic energy completely at each collision (inelastic collisions). Then, according to Drude, the mean excess velocity in one direction which is added by the field of force is $\frac{1}{2}a\bar{t}$ (zero at the beginning of the free path and $a\bar{t}$ at the end). Here the thermal velocity which is also present plays no role since it is directed equally often to the right and to the left. $\bar{t}$, the mean time between successive collisions, is equal to the mean free path divided by the mean velocity, being approximately

$$\bar{t} = \frac{\Lambda}{\sqrt{\left(\xi + \frac{a\bar{t}}{2}\right)^2 + \eta^2 + \zeta^2}} \cdot \tag{322}$$

In the cases occurring in practice, the added velocity is small in comparison to the thermal velocity. Therefore

$$\bar{t} = \frac{\Lambda}{w_\vartheta} \tag{323}$$

and

$$W_x = \frac{1}{2m}\frac{F_x\Lambda}{w_\vartheta} = \frac{1}{2m}\frac{1}{d^2\pi N_A c 2\sqrt{\frac{2kT}{m\pi}}}F_x. \tag{324}$$

The added velocity is seen to be proportional to F, the force. In this equation d signifies the sum of the radii of an ion and a gas molecule. Thus, the individually uniformly accelerated motions are reduced, as a result of the friction engendered by molecular collisions, to an average constant velocity proportional to F.

If, on the other hand, either the mean free path or the applied force is so large that the added velocity becomes large in comparison with the thermal velocity the motion between collisions can be considered as a motion with

[1] E. Riecke, *Wied. Ann.*, **66**, 376 (1898); P. Drude, *Ann. Physik*, **1**, 575 (1900).

constant acceleration and negligible initial velocity. The equations then become

$$\tfrac{1}{2}a\bar{t}^2 = \Lambda, \tag{325}$$

$$W_x = \sqrt{\frac{F_x}{2m}\Lambda} \tag{326}$$

and the velocity is seen to be proportional to the square root of the applied force.

The calculations have been made more rigorous, in particular by Lenard,[1] who has refined the deduction from the following viewpoint:

As has been pointed out by Jäger and by Jeans for the case of gas molecules, after an elastic collision on the average there still remains with the particles a part of their initial velocity. It can be shown that this fraction of the velocity W_i immediately before collision which stays with the colliding particles (velocity $= W_a$ immediately after collision) is

$$W_a = \frac{m}{m + m'} W_i \tag{327}$$

(m' large in comparison to m).[2] On the other hand

$$W_i = W_a + a\bar{t}, \tag{328}$$

whence

$$W_i = \frac{m + m'}{m'} a\bar{t}, \tag{329}$$

$$\overline{W} = \frac{\overline{W}_a + W_i}{2} = \frac{2m + m'}{2m'} a\bar{t}. \tag{330}$$

t is given by the equation

$$\bar{t} = \frac{\Lambda}{w'_\vartheta}\sqrt{\frac{m}{m + m'}}, \tag{331}$$

where the last factor appears because it is the relative velocity between the particles and the molecules which is of importance in determining the average time between two successive collisions.

Another correction is introduced by taking into account the fact that the particle collides more often with those molecules which are moving toward it than with those moving in its own direction of motion. For this reason it gives up more energy on the average than would be predicted by (327), wherefore $\overline{W}$ must be multiplied by the factor $\dfrac{3(m + m')}{3m' + 4m}$.

[1] P. Lenard, *Ann. Physik*, **3**, 312 (1900); **60**, 329 (1919).

[2] Cf. J. H. Jeans, The Dynamical Theory of Gases, p. 260 ff., Cambridge University Press (1925).

Finally there must be inserted the factor

$$\frac{2m}{2m + m'} + \frac{8}{\pi}\frac{m'}{2m + m'}$$

to give an approximate correction for the non-uniformity of the times between collisions. The final formula then becomes

$$\overline{W} = \frac{F\Lambda}{w'_\vartheta} \cdot \frac{1}{m'} \sqrt{\frac{m + m'}{m}} \frac{m + \frac{4}{\pi}m'}{\frac{4}{3}m + m'}. \tag{332}$$

The determining factors for the velocity of the ion are (1) it is proportional to the applied force; (2) it is inversely proportional to the density of the gas,

$$\Lambda = \frac{1}{cN_A\pi d^2};$$

and (3) if the particles are large in comparison with the gas molecules, $r \gg r'$, the velocity is inversely proportional to the cross section of the particle,

$$\frac{1}{\pi d^2} = \frac{1}{\pi(r + r')^2} \sim \frac{1}{\pi r^2}. \tag{333}$$

If the particle is spherical and large in comparison to the molecule but small in comparison to the mean free path,

$$m \gg m'$$

and

$$\Lambda \gg r \gg r',$$

the resistance offered to the motion of the particle equals the impressed force F and is

$$\frac{4\pi}{3} d^2 N_A c w'_\vartheta \overline{W} m'. \tag{334}$$

Throughout the foregoing discussion it has been assumed that the molecules are specularly reflected from the foreign body. This, of course, is only one of a number of possibilities. The other cases have been studied by Lenard (*loc. cit.*) and more thoroughly by Epstein.[1] Before proceeding to the other types of reactions between the particle and the gas molecules it is desirable to study in more detail the case of specular reflection. The resistance of the gas equals the momentum imparted to the sphere by the molecular impacts. This momentum can be divided into the part due to the impact of the molecule and that due to its rebound. It is then found that the latter part vanishes when summed over the sphere. This is possible because of the spherical shape

[1] P. Epstein, *Phys. Rev.*, **23**, 710 (1924).

of the particle. More molecules hit the forward hemisphere of the particle than the reverse because of the higher relative velocity (see p. 181) but those molecules which hit the forward hemisphere a glancing blow near the equator impart a forward momentum to the sphere *upon recoil*. On the other hand the recoil momentum could not vanish in the case of a moving plane (cf. p. 81). Accordingly the whole effect given by (334) is due to momentum of impact.

The next type of reaction between molecule and particle to be considered is as follows: The molecules stick to the surface and do not "evaporate" until a short interval of time has elapsed. During this interval the particle has turned irregularly [1] (Brownian motion) so that, on the average, the molecules evaporate uniformly in all directions. The recoil momentum therefore cancels out and the result is the same as before.

The final case to be considered is that of diffuse reflection described by Lambert's Cosine Law (intensity $\sim \cos\vartheta \sin\vartheta d\vartheta$). Two assumptions are still possible under this case. First, it might be assumed that the energy brought to any particular point on the sphere by impact must be removed by molecules hitting that point (thermally non-conducting sphere) or, secondly, that equalization of energy takes place throughout the sphere and all the molecules leave the sphere with the same average energy (perfect thermal conduction). In both cases there is a resultant recoil momentum, due to the fact that more molecules hit the forward side of the sphere than the reverse. The first assumption requires the insertion in equation (334) of the factor $\frac{\frac{4}{3}+\frac{3\pi}{16}}{\frac{4}{3}}$, the second requires the factor $\frac{\frac{4\pi}{3}+\frac{\pi^2}{6}}{\frac{4}{3}}$.

(*b*) *Large Spheres. The Stokes-Cunningham Law.* For the case of the motion of large spheres (i.e., large in comparison with the mean free path), the velocity is obtained from Stokes' Law,[2]

$$W = \frac{F}{6\pi r\eta}, \tag{335}$$

which is derived from the hydrodynamic equations applicable to this case.

Here again the velocity is directly proportional to the force but it is no longer inversely proportional to the cross section or the density of the gas as was the case with small spheres. In the present case the velocity is inversely proportional to the first power of the radius of the particle. The physical difference between the two cases is as follows: In the first instance of the *small* particles (or ions), it was assumed that the motion of the particle had no effect on the motion of the molecules in front of it prior to the actual collision. The

[1] G. Breit, *Phys. Rev.*, **23**, 608 (1924).

[2] G. Stokes, *Cambr. Phil. Soc. Trans.*, **9**, 5–8 (1856). Cf. also J. Weyssenhoff, *Ann. Physik*, **62**, 1 (1920).

situation is analogous to the flow of molecules through an opening small in comparison to the mean free path where all the molecules go through the opening which would have collided with the same area of the wall had the opening not been present, since the presence of the opening in no way affects the motion of the molecules in front of the opening. Similarly, if the particle is small in comparison to the mean free path, it is hit by just as many molecules as would hit an imaginary surface of area $\pi(r + r')^2$, and in these collisions the molecules have the same velocity that they would have upon colliding with the imaginary surface. Therefore the amount of momentum given to the particle is proportional to $\pi(r + r')^2$. In Stokes' case, however, the motion of the gas molecules is changed throughout the entire surrounding region by the motion of the particle. That is to say, so many molecules are reflected from the particle that they might be said to prepare the molecules in front of them, due to their altered distribution of velocities. The entire body of gas in front of the particle has therefore a component of velocity parallel to the velocity of the particle. The extent of this region increases with the size of the sphere. It therefore follows that the momentum transferred to the particle is no longer proportional to its cross section, but increases only with the first power of r.

Naturally, there must be a transition between the two cases (proportional to $1/r$ and $1/r^2$) and Cunningham has tried to find it[1] by taking into account the slip. With a finite coefficient of slip η/η_e one obtains from a hydrodynamic analysis the equation[2]

$$W = \frac{F}{6\pi\eta}\frac{1}{r}\frac{1 + 3\dfrac{\eta}{\eta_e r}}{1 + 2\dfrac{\eta}{\eta_e r}}. \tag{326}$$

If the slip is small ($\eta/\eta_e r < 1$); this approximates to

$$W = \frac{F}{6\pi\eta r}\left(1 + \frac{\eta}{\eta_e r}\right), \tag{337}$$

where according to Epstein (see below)

$$\frac{\eta}{\eta_e} = 0.7004\,\frac{2 - f}{f}\,\Lambda. \tag{338}$$

Epstein (*loc. cit.*) has deduced equation (337) from the kinetic theory by determining in a very noteworthy way the distribution function for the case of prescribed normal and tangential forces at the surface of the sphere. (The numerical coefficient 0.7004 appears in the more accurate calculation because η is set equal to $0.3502\rho w_3\Lambda$). This formula would seem to offer a transition to the value obtained from the gas theory for small spheres since for very small

[1] E. Cunningham, *Proc. Roy. Soc.*, **83A**, 357 (1910).

[2] See, for example, W. Lamb, Hydrodynamics, 4th ed., p. 593, Cambridge (1916).

values of r the quotient $(\eta/\eta_e r) \gg 1$ and therefore the resistance becomes, as it ought to be in this case, proportional to r^2. Actually, however, the series development is then not permissible and the exact formula (336) reduces for small values of r to $W = F/4\pi\eta r$ which is in contradiction to the direct deduction of (a) and to experimental evidence. The reason [1] for this is due to the fact that in the hydrodynamical treatment the momentum is considered to be imparted to the particles only by the components of velocity parallel to the surface (friction). This reasoning demands that the transfer of impulse vanish at the forward and back poles of the sphere while in the kinetic treatment it is just these collisions with the poles which are most important. In the method of hydrodynamics this last effect disappears since the propagation of pressure throughout the whole fluid equalizes these differences which occur only on account of the discontinuous structure of the gas (finite free path). In order to obtain the result for small spheres Cunningham starts out, not from the formal hydrodynamical equations, but from a consideration of the slip. His reasoning, however, seems unconvincing. He obtains the relation

$$W = \frac{F}{6\pi\eta r}\left(1 + 0.63\frac{\Lambda}{r}\right) \quad \text{or} \quad \left(1 + \frac{0.63}{2-f}\frac{\Lambda}{r}\right). \tag{339}$$

This would give a law of the desired form but the derivation is not rigorous, and other calculations give other results.[2]

A very interesting proof of (337) has been given by Epstein.[3] He uses the general method of p. 136 assuming that the deviations from Maxwell's distribution are small and writes accordingly for the distribution law

$$f = f_0\{1 - (A\xi + B\eta + c\zeta) - (L\xi^2 + M\eta^2 + N\zeta^2 + 2P\eta\zeta + 2Q\xi\zeta + 2R\xi\eta)\zeta\}, \tag{340}$$

where f_0 is Maxwell's Law, and $A, B, \ldots R$ small quantities. These are determined by setting up the equations of pressures and shearing stresses (viscosity) as due to transport of impulse

$$\left.\begin{aligned} p_{xx} &= -m\int f\xi^2 dw \ldots, \\ p_{yx} &= -m\int f\eta\xi dw \ldots, \qquad \text{etc.} \end{aligned}\right\} \tag{341}$$

The result is

$$f = f_0\left\{1 - \frac{m}{kT}[u\xi + v\eta + w\zeta] + \eta\frac{m^2}{k^2T^2\rho}\left[\frac{\partial u}{\partial x}\xi^2 + \frac{\partial v}{\partial y}\eta^2 + \frac{\partial w}{\partial z}\zeta^2 + \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right)\xi\eta + \left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}\right)\xi\zeta + \left(\frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}\right)\eta\zeta\right]\right\}, \tag{342}$$

with u, v, w as components of the bulk velocity of the gas. This leads to the

[1] Cf. R. A. Millikan, *Phys. Rev.*, (I) **32**, 382 (1911); (II) **21**, 217 (1923).
[2] L. W. McKeehan, *Physik. Z.*, **12**, 707 (1911).
[3] Epstein, *loc. cit.* See also R. A. Millikan, *Phys. Rev.*, **21**, 217 (1923).

hydrodynamical equation (336). In spite of the fact that equation (337) is valid for large r and equation (324) for small r, it is not necessary that the same numerical coefficient is kept during the whole transition.[1]

It seems possible that a large part of the difficulties encountered in the measurement of the electric charge on very small suspended particles may be traced to an unallowable extrapolation in the calculation of velocity measurements with equation (339).

Actually a measurement of the damping of vibrating spheres through a wide pressure range has led Knudsen and Weber to the equation

$$W = \frac{F}{6\pi\eta r}\left(1 + 0.68\frac{\Lambda}{r} + 0.35\frac{\Lambda}{r}e^{-1.85\frac{r}{\Lambda}}\right). \tag{343}$$

Shortly afterwards a similar result was obtained by Millikan[2] from an investigation of the motion of falling spheres. Further work gave him as the best expression of his results[3] obtained from a study of the fall of oil drops in air, in which the ratio Λ/r was varied from 0.1 to 134, the relation

$$W = \frac{F}{6\pi\eta r}\left[1 + \frac{\Lambda}{r}(0.864 + 0.29e^{-1.25\frac{r}{\Lambda}})\right]. \tag{344}$$

For large spheres this becomes

$$\frac{F}{6\pi\eta r}\left(1 + 0.864\frac{\Lambda}{r}\right) \tag{345}$$

and for small spheres

$$\frac{F}{6\pi\eta r}1.15\frac{\Lambda}{r}. \tag{346}$$

Millikan now points out that if this is compared first with the exact formula (337) for large spheres and second with the formula obtained from the gas theory for small spheres, the first comparison shows that

$$0.864 = 0.7004\frac{2-f}{f}. \tag{347}$$

From this it is found that f, the fraction of the molecules which are "emitted," is 0.895, while about 10 percent of the molecules are reflected. These figures are for oil drops in air. The coefficient for mercury droplets is 0.708 instead of 0.864 whence $f = 1$, for shellac, 1.078 ($f = 0.79$). For oil drops in hydrogen there was found the value 0.815 ($f = 0.925$), and in carbon dioxide, 0.82.

While the measurements with large spheres permitted the calculation of the accommodation coefficient, f, they gave no information as to whether the molecules are "reemitted," (i.e., leave the sphere only after a little time during

[1] See also M. v. Smoluchowski, Int. Math. Congr., 1912 (Cambridge, 1912).

[2] R. A. Millikan, Brit. Ass. Rep., p. 410, Dundee (1912).

[3] R. A. Millikan, *Phys. Rev.*, (II) **21**, 217 (1923); **22**, 1 (1923). Cf. also J. Mattauch, *Physik. Z.*, **25**, 620 (1924).

which the sphere has rotated) or whether they are diffusely deflected (leave the surface of the sphere isotropically with a Maxwellian distribution of velocities) at the point at which they collided. The reason for this is that in the region $r > \Lambda$ only tangential forces come into consideration and since in both of the above cases the departing molecules are distributed symmetrically about the normals to the surface, those tangential forces which are due to the departing molecules do not appear in either case. The entire force is due to the arriving molecules and those of the departing molecules which are elastically reflected. On the other hand, in the case of small particles (kinetic equation), it is the normal forces which are of significance. Millikan here compares his coefficient 1.154 with the magnitudes calculated by Lenard and Epstein for the same case. The latter are for the case of specular reflection and " reemission," 1.575 and for diffuse reflection at the point of collision, 1.131. Since 10 per cent are reflected ($1 - f = 0.1$) the remaining 90 per cent must obey the last named law which predicts the value 1.164 in comparison with the measured value 1.154.

The following table gives the values of the coefficients of external friction in CGS units for a number of gases at 1 atmosphere and about room temperature. Maxwell's f is also listed.

TABLE VI

Gas	Surface	Coefficient of Slip	f
H_2	Nickel [1]	110–140	—
Air	Nickel	80–100	—
CO_2	Nickel	50–60	—
CO_2	Old Shellac [2]	44	1
Air	Old Shellac	66	1
Air	New Shellac	97	0.79
Air	Polished Brass	75.4	—
Air	Mercury	66	1
Air	Oil	81.8	0.895
CO_2	Oil	50	0.92
H_2	Oil	—	0.925
He	Oil	—	0.875

[1] A. Timiriazeff, *Ann. Physik*, **40**, 971 (1913).

[2] L. J. Stacey, *Phys. Rev.*, (II) **21**, 239 (1923); K. S. van Dyke, *ibid.*, p. 250; R. A. Millikan, *ibid.*, p. 217; Y. Isida, *ibid.*, p. 550.

Heat Conduction at Moderate Pressures: The calculations of thermal conductivity are, with one exception, entirely analogous to those of viscosity. In the previous case, the quantity transported, namely the momentum mW in the X-direction, had nothing to do with the velocity of transport w in the Z-direction, and therefore the deviations from Maxwell's law noted in the preliminary remarks were slight. In the present case, however, the transported quantity is the kinetic energy $(m/2)w^2$, and this is directly connected

with the velocity of transport, which varies if the temperature gradient varies from point to point. The effect of this complication is to give one quite incorrect equation in the course of the argument if, in the simplified procedure which will be used here, the modification of the distribution is not taken into account.[1] The final result, however, is correct to the same degree, that is, to within a numerical factor, as in the case of viscosity. On the other hand, greater difficulties will present themselves on p. 205 in the discussion of radiometer forces.

Consider two plane surfaces of infinite extent placed parallel to the XY-plane. Between them is situated a gas of such density that the mean free path is small in comparison to the distance between the surfaces, d. The upper surface is maintained at the temperature T_2 and the lower at the temperature T_1. A linear temperature gradient will then be set up in the gas just as, when the surfaces were in motion, a linear velocity gradient was set up. In the layer of gas which is a distance z_0 from the bottom plate the temperature is (approximately, cf. below)

$$T_0 = T_1 + \frac{\partial T}{\partial z} z_0 = T_1 + \frac{T_2 - T_1}{d} z_0. \tag{348}$$

The molecular density at the same layer is $N_A c$ and the mean velocity of the molecules w_0 is that determined by the temperature T_0. The number of molecules flowing downward through 1 sq. cm. of this layer per second is, on the average,

$$N_A \frac{c_+ w_+}{6}. \tag{349}$$

These molecules come from a layer higher by a distance equal to the mean free path, Λ. w_+ and $N_A c_+$ are respectively the mean velocity and density prevailing in the higher layer. Similarly, there move upward in the same time through unit area of the layer

$$N_A \frac{c_- w_-}{6} \tag{350}$$

molecules which come from a layer lower by one free path.

Since there is no mass motion of the gas at the steady state (convection currents due to gravity have been eliminated by specifying that the colder plate is at the bottom) the number of molecules moving up must equal the number coming down in the same time, i.e.,

$$N_A \frac{c_+ w_+}{6} = N_A \frac{c_- w_-}{6}, \tag{351}$$

or the product cw must be constant throughout the gas This is the false formula already referred to, since it would lead to the conclusion that cw^2 is

[1] This fallacy is pointed out with especial emphasis by M. v. Smoluchowski, *Ann. Physik*, **35**, 997 (1911).

proportional to w, or that the pressure p ($= c(Mw^2/3)$; p. 77) changes throughout the temperature gradient due to proportionality with w or $\sqrt{T}$. This result is erroneous. As a matter of fact the formula just deduced is only applicable to the case of very low pressures where the collisions do not play a part in the process. At higher pressures there is no change in pressure along the temperature gradient (approximately, cf. p. 195). Hence the density is inversely proportional to the temperature ($c \sim 1/T$).

As has already been noted, the fact neglected in the argument is that the velocities of the molecules are no longer equally distributed over all directions. On the contrary there is an excess component of velocity in the direction of the decreasing z. The equality of the number of molecules moving down to the number moving up is caused by the fact that although the density c_+ of molecules coming from a higher layer is less, a larger proportion of these molecules moves downward. Accordingly c decreases with increasing z more rapidly than is to be expected from equation (351) so that the pressure remains constant as set forth above.

In any case the energy transported by each molecule coming from above is

$$\frac{1}{N_A} U_+ = \frac{1}{N_A}\left(U_0 + \Lambda \frac{\partial U}{\partial z} \right) = \frac{1}{N_A}\left(U_0 + \Lambda C_v \frac{\partial T}{\partial z} \right), \tag{352}$$

where C_v is the molar heat capacity at constant volume. Similarly the energy transported by molecules coming upwards is

$$\frac{1}{N_A} U_- = \frac{1}{N_A}\left(U_0 - \Lambda \frac{\partial U}{\partial z} \right) = \frac{1}{N_A}\left(U_0 - \Lambda C_v \frac{\partial T}{\partial z} \right). \tag{353}$$

If λ equals the thermal conductivity, that is, the amount of heat flowing per second through unit area under a temperature gradient of 1°/cm., the total heat flow across unit area of the layer of gas under consideration is

$$\lambda \frac{\partial T}{\partial z} = \frac{cw}{6} \cdot 2\Lambda C_v \frac{\partial T}{\partial z} = \frac{1}{3} wc\Lambda C_v \frac{\partial T}{\partial z} \tag{354}$$

or

$$\lambda = \frac{1}{3} wc\Lambda C_v = \eta \frac{C_v}{M} \quad \text{(cf. p. 133).}^1 \tag{355}$$

Equation (355) is extremely important. This proportionality between thermal conductivity and coefficient of viscosity

$$\lambda : \eta = C_v : M \tag{356}$$

is due to the fact that, in the first case, the flow of energy C_vT is measured by $\lambda(\partial T/\partial z)$ and in the second case, the flow of the momentum Mw, is measured by

[1] It follows from equation (355) that the thermal conductivity of a gas is independent of the pressure, subject to the same limitations as the analogous statement for the viscosity. Recent measurements by H. Gregory and C. T. Archer (*Phil. Mag.*, [7], 1, 593 (1926)) have confirmed this prediction of the theory.

$\eta(\partial W/\partial z)$, and that the mechanism of transport in the two cases is considered to be the same.

The formula is valid only so long as the kinetic energy of translation of the molecules alone contributes to C_v, accordingly, as long as $C_v = 3R/2$ (monatomic gases). As soon as other " degrees of freedom " such as rotation or vibration within the molecule are able to contribute to the specific heat, the argument becomes dubious, since, although at equilibrium it is true that the energy associated with these degrees of freedom is, on the average, proportional to the energy of the translatory motion, it is not certain whether the energy of rotation, etc. is exchanged upon collision in the layer under discussion as is the translational energy. This question has been discussed by Eucken.[1] An exact calculation by Chapman (p. 103) gives for monatomic, spherical molecules exerting an arbitrary central force the value

$$\lambda = 2.5 \frac{C_v}{M} \eta. \tag{357}$$

According to Enskog (*loc. cit.*) for rigid spheres

$$\lambda = 2.522 \frac{C_v}{M} \eta, \tag{358}$$

where η is given by (248). For rigid spheres with attractive forces the Sutherland correction (cf. p. 126) is somewhat greater for λ than for η, so that the term $1 + 0.036\ C/T$ appears in the denominator of (358).

The increase by the factor 2.5 is caused, according to Eucken, by the fact that those molecules which have an exceptionally high energy content transport this energy exceptionally quickly. In the analogous case of the transport of momentum this is not the case for the reasons just discussed. In the approximate deduction using the average speed w this fact also does not enter into the expression. The exact result, however, is that the mean velocity of the transport of energy is increased. The plausible assumption may now be made that the rotational energy possessed by any one molecule at a given instant is independent of the simultaneous value of the translational energy, so that a molecule may have a large rotational energy without possessing at the same time a particularly large velocity of translation. It is evident that a molecule in such a state would not have an increased speed of transport of energy and the reason for the factor 2.5 is therefore removed so that for diatomic molecules for which $C_{vt} = (3/2)R$ is the specific heat of translation and $C_{vr} = R$, that of rotation,

$$\lambda = \left(2.5 \times \frac{3}{2} + 1 \times 1\right) \frac{R}{M} \eta = \frac{19}{4} \frac{R}{M} \eta = 1.9 \frac{C_v}{M} \eta. \tag{359}$$

A compilation of the experimental data for the diatomic gases H_2, N_2, O_2,

[1] A. Eucken, *Physik Z.*, **14**, 324 (1913). (The assumption that a certain time for the equalization is necessary has been made by K. F. Herzfeld and F. O. Rice, *Phys. Rev.*, **31**, 691 (1928), to explain partly the absorption and dispersion of high frequency sound waves).

and NO gives values between 1.97 and 1.87. In this deduction it is assumed that the rotational energy of a molecule comes to equilibrium with the colder layer to which it has penetrated just as quickly as does the translational energy.[1] Eucken further states that that part of the specific heat due to vibrational energy C_s is to be taken into account by assuming that upon collision those components which are in the direction of motion are, in a certain sense, coupled with the velocity of the molecule so that the factor 2.5 holds also for this case but not for the other directions. As an example the equation for Cl_2 is found to be

$$\frac{\lambda M}{\eta C_v} = \frac{\left(2.5.\frac{3}{2}+1\times 1\right)R+\left(\frac{2.5}{3}+\frac{2}{3}\right)C_s}{\left(\frac{3}{2}+1\right)R+C_s} = 1.8 \qquad (360)$$

in comparison with the experimental value of 1.803.

Some gases, however (CO, CO_2, SO_2, H_2S, H_2), behave as if the exchange of the energies of rotation and vibration were not quick enough to take part in the conduction of heat. This seems to be true even of the energy of translation in the case of helium.

Pidduck [2] has attempted to calculate the heat exchange of a rotating molecule using the rigorous method of Chapman (p. 136). In order to retain the simplifications of a spherical molecule and at the same time to have the possibility of the exchange of energy of rotation, he assumes the molecules to be perfectly rough hard spheres. The effect of their being rough is to reverse the relative velocities of their points of contact upon collision. The radius of gyration of the molecule, or the ratio of this quantity to the molecular diameter then enters the formula aside from the molecular diameter and mass which regulate the number of collisions. If the entire mass of the molecule were concentrated at its center, this ratio would equal zero. For a homogeneous solid sphere it is 2/5, and for a sphere whose mass is concentrated in the outermost shell 2/3. The corresponding number with which the factor 2.5 of equation (357) is to be replaced is, for the three cases, 1.85, $\sim$ 1.85 and 1.71, which are in close agreement with Eucken's results.

Chapman [3] has generalized the model still further by considering the non-spherical shape of the diatomic molecule. To do this he assumes that the radius upon collision depends upon the velocities and orientations of the colliding molecules, the radius of gyration, however, is maintained constant. Practically, this calculation is only carried out for a definite relation between

[1] In a conversation with Professor Eucken the latter pointed out that if the transfer of rotational energy were slower than that of translational it might be compensated or overcompensated for by a possible "quantum restraint" (Quantenhemmung) (Chap. XVI), since this would cause a larger apparent mean free path.

[2] F. B. Pidduck, *Proc. Roy. Soc.*, **101A**, 101 (1922), following a proposal of G. H. Bryan, Brit. Assoc. Rep., 83 (1894).

[3] S. Chapman and W. Hainsworth, *Phil. Mag.*, **48**, 593 (1924).

the radius and the velocity, namely,

$$\frac{\text{Radius of Gyration}}{\text{Radius upon Collision}} = \sqrt{\frac{2}{3}\frac{1}{1+\frac{b}{|\tilde{w}|^{2s}}}}. \tag{361}$$

The calculation is extremely complicated but the constants in question, which depend on the constants b and s of the above formula, are evaluated numerically. The assumption of a collision radius which decreases with rise in temperature (closer approach of the colliding molecules) results naturally in a decrease in the number of collisions and therefore an increase in the mean free path (p. 126). This explains therefore the relation between viscosity and temperature (p. 156) without the necessity of the Sutherland attractive forces.

The thermal conductivity of mixtures is no more to be calculated additively from the corresponding values for the pure components than is the viscosity, since both depend upon the mean free path and this magnitude for one species of molecules is influenced by the presence of another species (p. 123).

In analogy to (259) the exact calculation of Enskog gives, for elastic spheres, if there are no diffusion processes,

$$\lambda = \frac{\lambda'\left(1+\beta_1'\frac{c}{c'}\right)+\lambda''\left(1+\beta_1\frac{c'}{c}\right)+A_1}{\left(1+\beta_1\frac{c'}{c}\right)\left(1+\beta_1'\frac{c}{c'}\right)-\frac{A_1^2}{4\lambda\lambda'}}, \tag{362}$$

where

$$\beta_1 = \left(\frac{d+d'}{2d}\right)^2\sqrt{\frac{2m'}{m+m'}}\,\frac{30m^2+16mm'+13m'^2}{8(m+m')^2}, \tag{363}$$

$$\beta_1' = \left(\frac{d+d'}{2d'}\right)^2\sqrt{\frac{2m}{m+m'}}\,\frac{13m^2+16mm'+30m'^2}{2(m+m')^2}, \tag{364}$$

$$A_1 = 27\sqrt{2\lambda\lambda'}\,\frac{(d+d')^2}{16dd'}\,\frac{(mm')^{5/4}}{(m+m')^{5/2}}. \tag{365}$$

Senftleben [1] has found that the thermal conductivity of a mixture of hydrogen and mercury vapor is changed if the mixture is radiated by light of wave-length 2537 Å. Cario and Franck [2] have shown that under such circumstances the hydrogen is partially dissociated by collisions of the second kind with mercury atoms excited by the ultra-violet light. The change in the thermal conductivity of the mixture therefore is due to a change in the composition of the mixture, part of the molecular hydrogen being converted into atomic hydrogen.

Long before this, Langmuir used the increased conductivity of heat from a tungsten filament heated in hydrogen as a measure of dissociation of the hydro-

[1] H. Senftleben, *Z. Physik*, **32**, 922 (1925).

[2] Cario and Franck, *Z. Physik*, **11**, 161; **12**, 162 (1922).

gen molecules into atoms.[1] Recently, formula (355) has been put to a new use. It has turned out that normal hydrogen is a mixture of two isomers, para-hydrogen and ortho-hydrogen, which have the same molecular weight and size of the molecule and so forth, but differ in their internal specific heats. Instead of measuring the specific heats directly, Bonhoeffer and Harteck [2] measured the thermal conductivity which is proportional to C_v, everything else being equal.

Heat Conduction at Low Pressures: Warburg [3] concluded that, at low pressures, there must take place a temperature discontinuity at the walls, in analogy to the slip. Smoluchowski [4] has studied the phenomenon experimentally and has given it a theoretical explanation. Recently Knudsen [5] has worked extensively with it. Other workers also have brought forth more abundant experimental material.[6] The treatment is formally identical with that of viscosity. Monatomic gases will first be discussed.

At low pressures, at which there are no collisions between molecules in the regions between the plates, formula (351) for the number of molecules moving upwards on the one hand and downwards on the other, which was found incorrect for dense gases, is valid. That is,

$$N_A \frac{c_+ w_+}{6} = N_A \frac{c_- w_-}{6}, \tag{366}$$

where $N_A c$ stands for the number of molecules per cc. Assuming complete heat exchange between molecule and plate, the amount of energy brought to the lower plate by molecules coming from above is

$$\frac{1}{N_A} C_v T_2 \quad \text{or} \quad \frac{1}{N_A} \int_0^{T_2} C_v dT, \tag{367}$$

if C_v varies with T. A corresponding equation holds for the molecules moving upwards. The flow of heat per square centimeter is then given by

$$\lambda \frac{\partial T}{\partial z} = \frac{cw}{6} C_v (T_2 - T_1). \tag{368}$$

The more exact calculation of p. 136 gives, upon substituting for w,

$$\lambda \frac{\partial T}{\partial z} = c C_v \sqrt{\frac{R}{2\pi M}} \sqrt{\frac{T_1 T_2}{T_1 + T_2}} (T_2 - T_1). \tag{369}$$

This formula has been applied to the measurement of low pressures by means of the hot wire manometer (Pirani Gauge) in which the heat conducted

[1] I. Langmuir, *J. Am. Chem. Soc.*, **34**, 860, (1912).

[2] Bonhoeffer and Harteck, *Z. physik. Chem.*, **4B**, 113, (1929).

[3] A. Kundt and E. Warburg, *Pogg. Ann.*, **156**, 177 (1875).

[4] M. v. Smoluchowski, *Wied. Ann.*, **64**, 101 (1898); *Wien. Ber.*, **107**, 304 (1898); **108**, 5 (1899); cf. also *Ann. Physik*, **35**, 983 (1911).

[5] M. Knudsen, *Ann. Physik*, **34**, 593 (1911).

[6] E. Gehrcke, *Ann. Physik*, **2**, 102 (1900); F. Soddy and A. J. Berry, *Proc. Roy. Soc.*, **83A**, 254 (1910); **84A**, 576 (1911).

away from a hot wire is measured by noting the input of electrical energy.[1]

In the general case there is, as before, a discontinuity in temperature at the plates. Assume that of all the molecules colliding with the plate the fraction f' assume the temperature of the particular plate (are adsorbed and reemitted) and the fraction $1 - f'$ are reflected without a change in their energy. Then the energy transferred to unit area of the plate by the fraction f' of the molecule is

$$f' \frac{cw}{6} \Delta U', \tag{370}$$

where $\Delta U' = C_v \Delta T'$ and is the difference between the energy prevailing at a layer a distance Λ away from the plate and the energy corresponding to the temperature of the plate itself.

The energy transfer must equal the flow of heat through the interior of the gas. Therefore, according to (355),

$$f' \frac{cw}{6} C_v \Delta T' = \frac{cw}{3} \Lambda C_v \frac{\partial T}{\partial z} = \lambda \frac{\partial T}{\partial z}, \tag{371}$$

$\partial T/\partial z$ may be evaluated from the fact that the temperature difference

$$(T_2 - \Delta T') - (T_1 + \Delta T') = T_2 - T_1 - 2\Delta T' \tag{372}$$

is distributed over the distance $d - 2\Lambda$, whence

$$\frac{\partial T}{\partial z} = \frac{T_2 - T_1}{d + 2\dfrac{2 - f'}{f'} \Lambda} \tag{373}$$

and the conduction of heat is given by

$$\lambda \frac{\partial T}{\partial z} = \lambda \frac{T_2 - T_1}{d + 2\dfrac{2 - f'}{f'} \Lambda}.[2] \tag{374}$$

[1] Pirani, *Verh. Deut. Phys. Ges.*, **4**, 686 (1906); Hale, *Trans. Am. Electrochem. Soc.*, **20**, 243 (1911); M. Knudsen, *Ann. Physik*, **35**, 389 (1911); **83**, 385 (1927). Other methods for measuring very low pressures employ (*a*) the Bourdon Spiral, (*b*) the ionization gauge and (*c*) the membrane manometer. (*a*) Johnson, *Z. physik. Chem.*, **61**, 457 (1908); Ladenburg and Lehmann, *Verh. Deut. Phys. Ges.*, **4**, 20 (1906). (*b*) Buckley, *Proc. Nat. Acad. Sci.*, **2**, 683 (1916); S. Dushman and Found, *Phys. Rev.*, **17**, 7 (1921); **23**, 734 (1924). (*c*) Scheel and Heuse, *Phys. Ber.*, **7**, 1 (1909). Cf. also S. Dushman, High Vacuum Technique; L. Dunnoyer, Vacuum Practice, Trans. by J. H. Smith, D. Van Nostrand Co. (1928). Finally the methods mentioned on p. 143 and p. 217. Cf. also H. Kamerlingh Onnes, Leiden Comm. Nr., 159 (1922).

[2] The decrease in flow of heat caused by the temperature discontinuity at the walls is the cause of the good insulating properties of porous substances. This is of great technical importance in lagging and packing between walls. The effect is large since the air spaces are so subdivided that d is not large in comparison to Λ. M. v. Smoluchowski, *Bull. Ac. Krak.*, p. 129 (1910).

The temperature discontinuity at the bottom plate is therefore

$$\left.\begin{aligned}\Delta T'' = \tfrac{1}{2}[\Delta T' + (1 - f')\Delta T' + f'.0] &= \frac{2 - f'}{2}\Delta T' \\ &= \frac{2 - f'}{f'}\Lambda\frac{\partial T}{\partial z}.\end{aligned}\right\} \tag{375}$$

The factor with which $\partial T/\partial z$ must be multiplied to obtain $\Delta T''$ is known as the coefficient of temperature discontinuity (Temperatursprung-koeffizient). It is here shown to be $(2 - f'/f')\Lambda$ and the more exact calculation confirms this value. For the case of two plane surfaces, Maxwell's assumption (p. 162) is equivalent to the postulate that all the molecules colliding with the surface rebound at the mean temperature T, where

$$T - T_1 = (1 - f')(T_0 - T_1) \tag{376}$$

and T_0 is their temperature just before collision with the surface. On the other hand Smoluchowski [1] has shown that there is a difference in the case of the flow of heat between two concentric cylinders. The experiments seem to contradict the assumption that all the reflected molecules have the same temperature.

Baule has applied his calculations, which were mentioned under coefficients of slip (p. 163), to the coefficient of temperature discontinuity. The fraction of the molecules $(1 - f)$ which is reflected from the first molecular layer of the solid wall is naturally the same as before, but the fraction (α') of the temperature difference which is retained by them is different from the fraction α of the excess velocity which was retained. Baule finds for monatomic molecules

$$\alpha' = \frac{m^2 + m^{*2}}{(m + m^*)^2}. \tag{377}$$

If the mass m of the gas molecule is small, α' is nearly unity so that the quantity

$$f + (1 - f)(1 - \alpha') = 1 - \alpha'(1 - f), \tag{378}$$

which appears in formulas (103–107) in the place of f', in this case equals f. This means that for, say hydrogen, the heat exchange with the walls is less complete than the exchange of velocity. If $m = m'$, both the fractions α and α' are equal to 1/2.

Thermal Effusion: The phenomenon of thermal effusion was predicted by Neumann [2] from a theoretical discussion. Feddersen [3] confirmed the predictions experimentally by showing that if two vessels are connected by a tube in which is placed a porous plug and if one end of the porous plug is warmed

[1] M. v. Smoluchowski, *Ann. Physik*, **35**, 983 (1911). In this article as in Knudsen's, there will be found a discussion of heat flow in vessels of different shapes.

[2] C. Neumann, *Ber. d. sächs. Akad. d. Wiss.*, **24**, 49 (1872).

[3] W. Feddersen, *Pogg. Ann.*, **148**, 308 (1873).

a pressure difference is developed between the two vessels, the higher pressurs appearing at the warm end. Violle,[1] however, raised against these experimente the objection that the results were invalidated by the presence of water vapor.

Reynolds[2] discovered the phenomenon independently of Feddersen, investigated it experimentally and was able to explain it on the grounds of the kinetic theory. Maxwell[3] has also considered the question and his general formula for the flow of a gas through a tube contains a term which depends on temperature gradients.

The theory is quite simple for the case of a tube whose diameter is small in comparison with the mean free path. The general equation (304) is then valid and at the steady state, when there is no flow, the left hand side equals zero, whence

$$\frac{p_2}{p_1} = \sqrt{\frac{T_2}{T_1}}. \tag{379}$$

Here the conditions are actually present which are described by the approximate calculation for large vessels (p. 188).

Nothing which is dependent on the form or nature of the connecting tube between the two vessels appears in the equation. The only condition that is demanded is that the diameter of the connecting tube be small in comparison with the mean free path. More recently Knudsen[4] has repeated the experiments, obtaining good agreement with the theory. Two vessels were connected through a sufficiently small tube or through a porous diaphragm. One of these vessels was heated, whereupon the pressure in that vessel increased. This increase can be caused by two different processes depending on the conditions of the experiment. If one of the vessels is heated throughout up to the mouth of the capillary, gas *leaves* the heated vessel and the density in the vessel decreases because the pressure increases less than the temperature.

$$c_2 = \frac{p_2}{RT_2} = c_1\sqrt{\frac{T_1}{T_2}}. \tag{380}$$

If, however, only the mouth of the capillary is heated just at the point where it enters vessel 2, the gas *enters* the latter vessel because it must then exert the same pressure p_2 as in the heated part of the capillary throughout the entire vessel 2 without changing the temperature in vessel 2.

The flow of a gas in mols through tubes whose diameters are large in comparison with the mean free path may be readily calculated, for the case in which there is no pressure gradient, as has been shown by Maxwell.

There pass from left to right, through the cross section $\pi d^2/4$,

$$\frac{\pi d^2}{4} N_A \frac{c_1 w_1}{4} = \frac{\pi d^2}{4}\frac{N_A}{4}\left(cw - \Lambda\frac{\partial cw}{\partial x}\right) \tag{381}$$

[1] T. Violle, *Journ. d. Phys.*, **4**, 97 (1875).
[2] O. Reynolds, *loc. cit.*
[3] Clerk Maxwell, *loc. cit.*
[4] M. Knudsen, *Ann. Physik*, **31**, 205, 633 (1910).

molecules which come from the distance Λ. Similarly, there come from right to left

$$\frac{\pi d^2}{4}\frac{N_A}{4}\left(cw + \Lambda\frac{\partial cw}{\partial x}\right). \tag{382}$$

The excess flow from right to left is therefore

$$\frac{\pi d^2}{4}\frac{N_A}{4}\cdot 2\Lambda\frac{\partial cw}{\partial x}. \tag{383}$$

Since there is no pressure gradient, p is constant throughout, and cw^2 is everywhere constant. Therefore

$$\frac{\partial}{\partial x}(cw) = \frac{\partial}{\partial x}\left(\frac{cw^2}{w}\right) = cw^2\frac{\partial}{\partial x}\frac{1}{w} = -cw\frac{1}{w}\frac{\partial w}{\partial x} = -cw\frac{\partial lnw}{\partial x}$$
$$= -\frac{cw}{2}\frac{\partial lnT}{\partial x}. \tag{384}$$

The stream of molecules going from right to left is then given by

$$\frac{\pi d^2}{4}\frac{N_A}{4}2\Lambda\left(-\frac{cw}{2}\frac{\partial lnT}{\partial x}\right) = -\frac{\pi d^2}{4}\frac{M}{4m}cw\Lambda\frac{1}{T}\frac{\partial T}{\partial x} = -\frac{\pi d^2}{4}\frac{3}{4m}\eta\frac{1}{T}\frac{\partial T}{\partial x} \tag{385}$$

or, expressed in mols,

$$-\frac{\pi d^2}{4}\frac{3}{4M}\eta\frac{1}{T}\frac{\partial T}{\partial x}. \tag{386}$$

The temperature gradient therefore produces a flow such that gas flows *up* the gradient.

Upon adding this term (386) to the right hand side of the equation of flow (313) there is obtained an expression for the flow in the most general case involving both temperature and pressure changes. The pressure gradient in the stationary state (zero flow) can then be obtained by setting the left hand side equal to zero. Then for $d > \Lambda$

$$\frac{dp}{dT} = \frac{6\eta^2 R}{Mp}\frac{1}{\frac{d^2}{4} + 4\frac{\eta}{\eta_e}\frac{d}{2}}. \tag{387}$$

The formulas treated above are of great practical importance in the measurement of the pressure in a vessel by means of a manometer which is at a different temperature. Except for high pressures, the pressure read at the manometer will not be the true pressure in the vessel. The correction is easy to make only in two extreme cases. The simpler case is present if the diameter of the tubes connecting the vessel with the manometer is everywhere small compared with the mean free path. In this case the distribution of the temperature along the tube does not matter, but only the temperature at the two ends. Formula 379 can then be used directly. The other extreme case requires

that the mean free path be small throughout when compared with the diameter of the vessel. In this case formula 387 must be used. If the diameter of the tube is uniform, the distribution of temperatures is again of no importance. Even then the application of this equation to experimental data involving large temperature intervals is attended by mathematical difficulties since in this case the dependency of η upon T and of η/η_e upon p and T must be taken into account. A graphical method of integration has been used by Wilson.[1]

In Wilson's case, a vessel containing He at about 1500° K. was connected by an 8 mm. tube to a manometer at room temperature. If a pressure of 0.389 mm. was read on this manometer, formula (388) would give a pressure in the vessel of 0.496. The exact calculation by the graphical method gives 0.566, and the experiment (rate of flow through small opening) 0.572.

Knudsen deduces a somewhat more complicated formula in which the factor 6.1 takes the place of 4 in the coefficient of the slip. The entire expression is preceded by a somewhat smaller coefficient and the change in Λ with the temperature according to Sutherland (pp. 126–128) is taken into account.

In a tube closed at each end the total gas flow produced by the pressure gradient is, on the average, compensated by the flow produced by the temperature gradient. This, however, cannot be the case at each point in the cross section of the tube because the Poiseuille flow is essentially greater at the middle of the tube than at the periphery. Therefore, at the center of the tube, the action of the pressure gradient will dominate and, at the rim, the action of the temperature gradient. Since the total flow is zero there will be a flow along the walls toward the higher temperature and another at the center toward the lower.

For high pressures equation (387) may be integrated (neglecting η/η_e) with the result

$$p_2^2 - p_1^2 = \frac{6\eta_0^2}{\frac{d^2}{4} T_0} \frac{R}{M} (T_2^2 - T_1^2). \tag{388}$$

Knudsen [2] has tested this formula (taking into account the dependence of Λ upon the temperature) and has found that the best agreement is obtained with the factor 7.4 instead of 6. In one experiment ten tubes 5 cm. long and 0.374 mm. in diameter were connected to each other through wide tubes, so that the pressure differences were added as are the potential differences of galvanic elements connected in series. The left end of each capillary was heated electrically to about 380° C., and the right end of each maintained at about 50° C. Hydrogen at atmospheric pressure in this apparatus gave a total pressure difference of 0.039 mm. of Hg (calc. 0.034). At an average pressure of 6.69 mm. the pressure difference was 1.93 (calc. 2.04). More recently Knudsen [3] has extended equation (387) to the pressure region through-

[1] C. Wilson, *Phys. Rev.*, **33**, 851 (1929).
[2] M. Knudsen, *Ann. Physik*, **33**, 1435 (1910).
[3] M. Knudsen, *Ann. Physik*, **83**, 797 (1927).

out which the mean free path is of the same order of magnitude as the radius of the tube, and has checked his deductions experimentally.

If the ends of a capillary are connected by means of a wide glass tube, a steady current of gas may be maintained by heating one end of the capillary. This is somewhat analogous to thermo-electric currents.

There is also the converse effect. Dufour [1] has found that upon diffusion through a porous plate (for example, of hydrogen into a vessel containing air) the temperature at the inlet side is raised.

Knudsen [2] has repeated these experiments also. Upon streaming air through a glass tube in which was placed a plug of glass wool he found a temperature increase at the inlet end. With hydrogen at an inlet pressure of 2.6 mm. and a pressure difference of 2.54 mm., this amounted to about 0.06° and at the inlet pressure of 171 mm. and a pressure difference of 11 mm., to about 0.62°. At the outlet the gas has returned to its initial temperature wherefore Knudsen concludes that the effect is not due to a Joule-Thomsen heating. In contradiction to this last statement Dufour has found a temperature drop in the space into which the hydrogen left the capillary.

Weber [3] has ascribed this phenomenon to the fact that in the Poiseuille flow of a gas each molecule carries, on the average, an energy equal to $(5/2)kT$. In the uniform flow of a gas, the distribution formula is

$$dN = N_0 \sqrt{\frac{m}{2\pi kT}}^3 e^{-\frac{m}{2kT}[(\xi-\xi_0)^2+\eta^2+\zeta^2]} d\xi d\eta d\zeta. \tag{389}$$

The average energy transported per molecule, passing through 1 sq. cm per sec is

$$\left.\begin{aligned} \bar{\epsilon} &= \frac{\int_{-\infty}^{+\infty} \frac{m}{2}(\xi^2+\eta^2+\zeta^2)\xi dN}{\int_{-\infty}^{+\infty} \xi dN} \\ &= \frac{\frac{m}{2}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \xi(\xi^2+\eta^2+\zeta^2) e^{-\frac{m}{2kT}[(\xi-\xi_0)^2+\eta^2+\zeta^2]} d\xi d\eta d\zeta}{\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \xi e^{-\frac{m}{2kT}[(\xi-\xi_0)^2+\eta^2+\zeta^2]} d\xi d\eta d\zeta} \\ &= \frac{5}{2}kT \end{aligned}\right\} \tag{390}$$

In the evaluation of this integral all terms containing powers of ξ_0 higher than the first are neglected since $\xi_0 << \xi$

This $(5/2)kT$ is composed of thermal kinetic energy $((3/2)kT)$ and mechanical energy $(pv/N = kT)$. If the conditions of molecular flow obtain, the average

[1] L. Dufour, *Arch. de sci. phys. et nat. Genf.*, **45**, 9 (1872); *Pogg. Ann.*, **148**, 490 (1873).

[2] M. Knudsen, Kongress Solvay 1911, *Deutsche Ausgabe als Abh., d.D. Bunsen-Ges.*, **3**, 116, Halle (1913).

[3] S. Weber, *Z. Physik*, **24**, 267 (1924).

energy carried per molecule is only $(4/2)kT$, as then the distribution is undisturbed, and the energy transport is given by

$$\left.\begin{aligned}\bar{\epsilon} &= \frac{\int \frac{m}{2}(\xi^2+\eta^2+\zeta^2)\xi dN'}{\int \xi dN'} \\ &= \frac{\frac{m}{2}\int_0^\infty\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\xi(\xi^2+\eta^2+\zeta^2)e^{-\frac{m}{2kT}(\xi^2+\eta^2+\zeta^2)}d\xi d\eta d\zeta}{\int_0^\infty\int_{-\infty}^{\infty}\int_{-\infty}^{+\infty}\xi e^{-\frac{m}{2kT}(\xi^2+\eta^2+\zeta^2)}d\xi d\eta d\zeta} \\ &= \frac{4}{2}kT\end{aligned}\right\} \quad (391)$$

Since

$$dN' = N_0\sqrt{\frac{m}{2\pi kT}}^3 e^{-\frac{m}{2kT}(\xi^2+\eta^2+\zeta^2)}d\xi d\eta d\zeta. \quad (392)$$

That it is larger than $(3/2)kT$ in both cases, comes from the fact that the molecules with more energy travel faster. The integration with respect to ξ is carried from $-\infty$ to ∞ in equation (390) and from 0 to ∞ in equation (391) because in the former case the distribution function accounts for the one sided flow $(\xi - \xi_0)$ with a constant N_0, while in the latter case it does not, but the flow is determined by the variation of N_0. To give the distribution in the case of molecular flow, one ought to say that at any place the distribution is made up by N_- molecules with a ξ between 0 and ∞ going from left to right and N_+ molecules with ξ between 0 and $-\infty$ going from right to left.

From the foregoing discussion it follows that at a point at which the flow changes from Poiseuille to molecular, energy is lost by the gas and must appear as heat in the surroundings. Such a transition in the type of flow is caused by the presence of the porous plug. Conversely, the outlet end of the plug gets colder. The difference for the two types of flow may be ascribed to the fact that there is no mass motion of the gas in its molecular flow.

Radiometer Forces at Low Pressures: It has been found that solid objects may experience unbalanced forces when surrounded by a gas which is not in thermal equilibrium. Such forces, aside from those caused by convection currents, are known as radiometer forces. The name is due to the fact that in the earlier experiments on the subject the disturbance of the thermal equilibrium (i.e. non-uniform temperature distribution) was produced by radiation. These radiometric forces vary greatly with the gas pressure (see below). Here again the theoretical treatment of the phenomena will be facilitated by considering separately the cases of low and high pressures. As before, the criterion of the magnitude of the pressure is the length of the mean free path. If this is large in comparison with the important dimensions of the

apparatus, the pressure is "low" and vice versa. Knudsen [1] has shown that the relations are particularly simple in the case of very low pressures. Two parallel plates are placed opposite each other in a vessel, the walls of which are at the temperature T_1. One of the plates is maintained at the temperature T_1 and the other at the temperature T_2. If the mean free path is large in comparison to all the dimensions of importance (distance from the plates to the walls and the distance between the plates) only collisions of the molecules with solid surfaces come into account and the velocity of each molecule is determined by the temperature of the surface from which it comes. Since a stationary state is assumed, the same number of molecules must pass each sq. cm. in opposite directions throughout, i.e., the number of collisions per second on unit surface must be constant at all points. Let $N_A c$ be the density of the molecules in the undisturbed gas, that is, in the gas between the plate of temperature T_1 and the outer wall which is at the same temperature. The number of collisions on the plate due to molecules coming from the outer wall is then $N_A c w_1/6$ and the pressure exerted equals the gas pressure $p = Mcw_1^2/3$. Let $N_A c_1$ equal the density of the molecules in the region between the plates which move from plate 1 to plate 2 with the velocity w_1 and $N_A c_2$ be the density of these moving from 2 to 1 with the velocity w_2. Then the total density between the plates is $3N_A(c_1 + c_2)$. Due to the fact that there are the same number of collisions per second upon unit area of all the surfaces involved

$$c_1 w_1 = c_2 w_2 = \frac{cw_1}{6}. \tag{393}$$

The pressure exerted [2] on that side of plate 1 which faces plate 2 is

$$\left.\begin{aligned} c_1 M w_1^2 + c_2 M w_2^2 = c_1 M w_1 (w_1 + w_2) &= \frac{cMw_1}{6}(w_1 + w_2) \\ = \frac{cMw_1^2}{6}\left(1 + \frac{w_2}{w_1}\right) &= \frac{p}{2}\left(1 + \sqrt{\frac{T_2}{T_1}}\right). \end{aligned}\right\} \tag{394}$$

The excess pressure on plate 1 which tends to force it away from plate 2 is therefore [3]

$$P = \frac{p}{2}\left(\sqrt{\frac{T_2}{T_1}} + 1\right) - p = \frac{p}{2}\left(\sqrt{\frac{T_2}{T_1}} - 1\right). \tag{395}$$

If plate 1 is movable P can be measured and (395) be used to calculate p, the gas pressure. The measurement is independent of the nature of the gas,

[1] M. Knudsen, *Ann. Physik*, **32**, 809 (1910); **34**, 823 (1911); M. v. Smoluchowski, ibid., **34**, 182 (1911); **35**, 983 (1911).

[2] The first term on the left of this equation signifies the pressure exerted by the *recoil* of molecules from plate 1, the second term the pressure due to the *impact* of molecules on plate 1.

[3] This equation had been previously obtained by Reynolds.

being equally applicable to vapors of mercury or those coming from stop-cock grease. In this respect this method is preferable to the McLeod gauge. The force P can be increased by increasing the temperature difference. Plate 2 experiences no unbalanced force since it is confronted on both sides by cold surfaces (plate 1 and wall of the vessel). The reaction (excess pressure) of the force acting on plate 1 is supplied by the wall of the vessel opposite plate 2.

It has so far been assumed that the molecules acquire the temperature of the plate immediately upon collision with the plate. It will now be shown that equation (395) is independent of this assumption.

Maxwell's assumption that the fraction $1 - f$ of the molecules is reflected without change in energy and that the fraction f is emitted at the temperature of the emitting plate leads to the following equations: Both the group of molecules moving from 1 to 2 as well as the group of molecules moving from 2 to 1 contain molecules which are at the temperature of plate 2 and molecules which are at the temperature of plate 1. The total number of molecules passing per second through any cross section must equal the number passing in the same time in the opposite direction. Therefore

$$c_2^{\downarrow} w_2 + c_1^{\downarrow} w_1 = c_2^{\uparrow} w_2 + c_1^{\uparrow} w_1. \tag{396}$$

The $N_A c_2^{\downarrow} w_2$ molecules leaving plate 1 per second with the velocity w_2 corresponding to the temperature of plate 2 constitute the reflected fraction $(1 - f)$ of $N_A c_2^{\downarrow} w_2$ molecules colliding with plate 1 with this velocity, for the $N_A c_1^{\downarrow} w_1$ molecules which have already the velocity w_1 corresponding to plate 1 before collision naturally will not change their energy upon collision with plate 1. Hence

$$c_2^{\uparrow} w_2 = (1 - f) c_2^{\downarrow} w_2. \tag{397}$$

Similarly at the upper plate

$$(1 - f) c_1^{\uparrow} w_1 = c_1^{\downarrow} w_1. \tag{398}$$

Substitution in (396) gives

$$c_2^{\uparrow} w_2 = c_1^{\downarrow} w_2 \qquad \text{and} \qquad c_2^{\downarrow} w_2 = c_1^{\uparrow} w_1. \tag{399}$$

Furthermore, the total number of collisions with plate 1 is, as before,

$$c_1^{\downarrow} w_1 + c_2^{\downarrow} w_2 = \frac{c w_1}{6}. \tag{393'}$$

Upon substitution of all the various quantities the total excess pressure is seen to have the same value as before,

$$M\left(c_2^{\downarrow} w_2^2 + c_1^{\downarrow} w_1^2 + c_2^{\uparrow} w_2^2 + c_1^{\uparrow} w_1^2 - \frac{2 c w_1^2}{6}\right) = \frac{p}{2}\left(\sqrt{\frac{T_2}{T_1}} - 1\right). \tag{400}$$

On the other hand a complicated result is obtained from the assumption that each molecule exchanges energy on colliding with the walls, but does not do so completely, or if f is assumed to depend upon the temperature.[1]

[1] M. v. Smoluchowski, *Ann. Physik*, **34**, 182, 383 (1911).

It must be emphasized that, at *low* pressures, the radiometer force is always directly proportional to the pressure. The relation between the force and the temperature, however, will vary with the type of apparatus, equation (395) expressing the behavior only of the type for which it was deduced, namely, two parallel plates at different temperatures. Rubinowicz [1] has calculated the force exerted on a sphere of non-uniform temperature in an attenuated gas. Debye [2] has used the deviations from Knudsen's equation for radiometer forces at low pressures, which is derived from the assumption of no collisions between molecules, to calculate the diameters of the gas molecules. In this way he finds the diameters of H_2 and O_2 to be 2.9 and 3.9 Å respectively. These values are in fair agreement with those obtained by other methods.

The Absolute Manometer: Knudsen has applied the results of the last paragraph to the measurement of low pressures. Since, as pointed out above, the radiometer force is in this case independent of the nature of the gas, the instrument is called the "absolute manometer." It can be used to measure condensable vapors which are not recorded by the McLeod gauge.[3] Knudsen has described several forms of his manometer. Fig. 26 is a plan of a type which is suitable for absolute measurements. A copper cylinder A', 1.63 cm. in diameter, is set in a glass bell jar which can be evacuated. The bell jar is lined with a blackened metal tube C in order to promote uniformity of temperature. The polished base of the copper cylinder is heated electrically, thus constituting the hot plate. The cylinder is provided with the thermometer T' and, to give a sharp limit to the flow of heat, it is surrounded with a copper block B, the distance between the two being 0.174 mm. The block B has the temperature of the surroundings (thermometer T''''). The action of B is similar to that of the guard ring of a condenser. A copper plate A'', provided with the thermometer T'', is suspended in front of the base of the heated copper cylinder by means of a platinum wire 0.1 mm. in diameter. The distance between A' and A'' is 0.12 mm., the effective area 2.1 sq. cm. and the distance from the supporting wire to the mid point of the hot plate is 1.2 cm. The angular displacement of the plate is measured at a known temperature difference. With a temperature difference of 46° a pressure of hydrogen equal to 0.002 mm. Hg gives a deflection of a beam of light reflected from a mirror on the moving plate equal to 4 mm. Deviations from the simple formula set in at pressures greater than 0.006 mm. Another type of the instrument which is suited for relative measurements is shown in Fig. 27.[4] Half of the

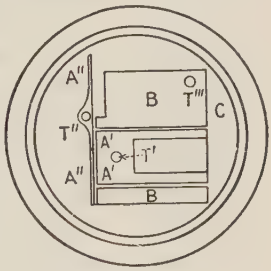

FIG. 26

[1] Rubinowicz, *Ann. Physik*, **62**, 691 (1920).

[2] P. Debye, *Physik. Z.*, **11**, 1115, 1260 (1910).

[3] This must not be confused with the hot wire manometer (Pirani Gauge) which measures thermal conductivity (p. 194).

[4] M. Knudsen, *Ann. Physik.*, **44**, 525 (1914).

wall of a metal tube A is cut away leaving a window behind which there is hung at C an aluminum leaf about 0.5μ thick and 10 cm. long. This leaf serves as plate 1. The inside of the surrounding glass tube G is silvered and serves as the hot plate 2. It is heated by means of a jacket through which hot water can be passed. The metal tube A protects one side of the aluminum leaf from collision with hot molecules, thereby taking the place of the "wall of the containing vessel" of the general theory. The displacement of the leaf is measured by means of a microscope through the window D. With a temperature difference of 50° and a pressure of 1.5×10^7 mm. the deflection amounts to 1/200 mm. Obviously the instrument cannot be operated for such a long time that A too becomes warm.[1]

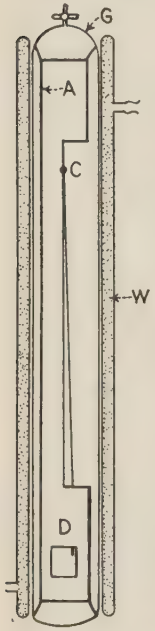

FIG. 27.

Radiometer Forces at High Pressures: Fresnel[2] was the first to note that bodies suspended in an attenuated gas receded upon irradiation. Crookes[3] investigated this phenomenon and constructed the radiometer which is usually seen as a scientific toy, but which in the improved form, due to Nichols and others,[4] can be used to measure the amount of incident radiant energy. Light metallic vanes are mounted on an axis and the whole placed in an evacuated glass bulb. One side of each of the vanes is polished and the other side is blackened.[5] A quantitative experimental investigation showed Crookes that the force is proportional to the intensity of the incident radiation and dependent upon the gas pressure within the bulb. He had already attempted to explain the phenomenon by saying that the light is more strongly absorbed on the blackened side; this side is therefore warmer and the molecules exert a greater pressure upon it. But, as Crookes himself realized, this explanation is false since it neglects the fact that at high pressures the number of collisions with the hot side is less than the number on the cold side by the factor $1/\sqrt{T}$. This just compensates the effect of the increased velocity ($\sim \sqrt{T}$). Schuster[6] found that the surrounding gas has a momentum equal and opposite to that of the vanes so that there is no force acting on the center of gravity of the whole system. Hence, the phenomenon is not due to the pressure of the

[1] For a more detailed description of the construction and use of the absolute manometer see E. v. Angerer, *Ann. Physik*, **41**, 10 (1913); Woodrow, Phys. Rev., **4**, 491 (1914); Shrader and Sherwood, *ibid.*, **12**, 70 (1918); S. Dushman, Production and Measurement of High Vacuum, Schenectady 1922; L. Dunoyer, Vacuum Practice, trans. by J. H. Smith, D. Van Nostrand Co. (1928).

[2] A. Fresnel, *Ann. chim. phys.*, **29**, 57, 107 (1825).

[3] W. Crookes, Phil. Trans., **164**, 501 (1874); **166**, 340 (1876); **170**, 132 (1880).

[4] E. F. Nichols, *Wied. Ann.*, **60**, 401 (1897); E. Pringsheim, *ibid.*, **18**, 32 (1883): Cf. also W. Donle, *ibid.*, **68**, 306 (1899); B. J. Spence, *J. Opt. Soc. Am.*, **6**, 625 (1922); E. Nichols and J. Tear, *Phys. Rev.*, **21**, 587 (1923); O. Sandrik, *J. Opt. Soc. Am.*, **12**, 355 (1926).

[5] The arrangement is similar to an anemometer, the light taking the place of the wind.

[6] A. Schuster, *Phil. Trans.*, **166**, 715 (1880).

radiation. Furthermore, O. Reynolds [1] soon carried out measurements and emphasized that there is an optimum value of the pressure which is determined by the ratio of the dimensions of the vanes to the mean free path.

The subject has received renewed attention through the observations of Ehrenhaft [2] who found that when small particles (of the order of 10^{-6} to 10^{-4} cm. in diameter) floating in a gas, are intensely irradiated, a motion of the particle is set up which may be either in the direction of the light ray (positive photophoresis in the case of Au, Ag, Hg) or in the opposite direction (negative photophoresis, in the case of S, Se, I, Bi). Since a direct action of the light (radiation pressure) could only result in a positive photophoresis,[3] the effect must be caused by the gas. The theory was developed by Rubinowicz, Zerner and others.

Gerlach and Westphal [4] have made exact measurements in which light was allowed to fall on a vane of thin metal foil. They found that as the gas pressure is increased the radiometer force passes through a maximum at from 10^{-2} to 10^{-1} mm. Hg. The position of this maximum was found to depend on the nature of the gas. Further experiments by Gerlach [5] showed that the force is directly proportional to the intensity of the illumination.

Czerny and Hettner [6] have shown that, at pressures where the mean free path is small in comparison to the dimensions of the apparatus (i.e. on the high pressure side of the maximum in the pressure-force curve) the forces are inversely proportional to the pressure of the surrounding gas. Gerlach and Westphal (*loc. cit.*) have also observed Ehrenhaft's negative effect. Thus, at high pressures, some radiometer vanes move *toward* the light source rather than away from it.

The theoretical treatment of this subject was not developed with any degree of success until comparatively recently. The earlier investigations [7] led to equations which in some cases were not even in qualitative agreement with the experimental data. In some developments the disagreement is due to the fact that although the calculated forces are probably present, they are negligible in comparison to other forces which were not taken into account. Maxwell first attacked the problem quantitatively according to the method indicated on p. 136. He determined the distribution function of molecules which repel each other with an inverse fifth power in which case, as in other problems,

[1] O. Reynolds, *ibid.*, **166**, 727 (1880).

[2] F. Ehrenhaft, *Ann. Physik*, **56**, 81 (1918); J. Parankiewicz, *ibid.*, **57**, 489 (1918).

[3] P. Epstein, *Mitt. Phys. Ges. Zurich*, **19**, 30 (1919).

[4] W. Gerlach and W. Westphal, *Verh. deut. physik. Ges.*, **21**, 218 (1919); W. Westphal, *Z. Physik*, **1**, 92, 431 (1920); **4**, 221 (1920); W. Gerlach, *ibid.*, **2**, 207 (1920).

[5] W. Gerlach and H. Albach, *ibid.*, **14**, 285 (1923); W. Gerlach and A. Golsen, *ibid.*, **15**, 1 (1923); W. Gerlach and E. Madelung, *ibid.*, **21**, 254 (1924).

[6] Czerny and Hettner, *Z. Physik*, **30**, 258 (1924).

[7] C. Maxwell, *Phil. Trans.*, **170**, 231 (1880); Scientific Papers **2**, 681, Cambridge (1890) O. Reynolds, *Phil. Trans.*, **170**, 727 (1880); *Phil. Mag.*, **11**, 385 (1881); Scientific Papers, vol. I, 257, 384. Cambridge (1900); G. Laski and F. Zerner, *Z. Physik*, **3**, 224 (1920); **6**, 411 (1921); E. Einstein, *Ann. Physik*, **69**, 241 (1922); T. Sexl, *ibid.*, **80**, 515 (1926); **81**, 800 (1926); A. Sterntal, *Z. Physik*, **39**, 341 (1926).

the calculations are relatively simple.[1] He carries the development of the distribution function

$$f = f_0(1 + \alpha\xi + \ldots) \tag{401}$$

to terms in the third power of the velocities. It is then found that there are pressures normal to the vane which depend upon the second differential quotient of the temperature ($\Delta_2 T$) at the point in question. These would readily explain the forces on a radiometer. However, if the gas is assumed to be at rest, they are exactly compensated by forces tangential to the edges so that there is no force acting on the body as a whole. Maxwell explained the presence of radiometer forces qualitatively by stating that at the surface of solid bodies in the presence of tangential forces the gas is not at rest, but has a finite slip velocity so that the tangential forces are decreased and there is no longer the former compensation. Favorable evidence for the explanation is afforded at low pressures where the slip is enormous and may be calculated with certainty. In this case the calculations give the correct results (absolute manometer, see the preceding section).

Almost simultaneously with Maxwell, Reynolds[2] attempted to develop the theory of radiometer forces. The noteworthy idea which he added to the problem was that thermal effusion and radiometer forces are evidences of the same phenomenon. If the solid body (tube) is immovable, only the gas is set in motion by the temperature gradient. In radiometers the solid body also may move. He first emphasized that a temperature difference gives no resultant force on infinitely large plates, but that the action takes place at the edges of the vanes due to the divergence of the lines of flow of heat. As in the case of Maxwell's treatment the second differential quotient of the temperature is the determining factor which seems in contradiction to the experimental proportionality to the first derivative. Reynolds, however, has taken into account the slip at the outset in his formulae by assuming the "length of transport interval" to be different in the vicinity of a solid body and in the interior of the gas. In this manner he arrives at a total force which is different from zero.

The first simple discussion leading to an accurate result was given by A. Einstein[3] The development is approximate and only attempts to give a qualitative description which will be correct to within the order of magnitude. In order to simplify the problem as much as possible, Einstein limits himself to radiometric forces produced by a flow of heat rather than light. He considers a linear homogeneous flow of heat to be established in the gas under consideration. Then, since the arrangement is such as to preclude convection currents the number of molecules moving along any given direction[4] $(cN_A|\overline{w}|)/6$ is constant. Any large surface in the gas, however, experiences a constant

[1] Clerk Maxwell, *loc. cit.*

[2] O. Reynolds, *loc. cit.*

[3] A. Einstein, *Z. Physik*, **27**, 1 (1924).

[4] This consideration cannot be exact (p. 188) as it would lead to pressure differences in the gas.

pressure ($\sim cN_A|\overline{w}|^2$). Thus, through the body of the gas, there is an equilibrium of flow ($c|\overline{w}|$ = constant) and at the material surfaces there is equilibrium of pressure ($c|\overline{w}|^2$ = constant). If a vane is placed in the gas perpendicular to the direction of the flow of heat the pressure will be constant over its surface except for a region at the edge of the vane in which there is a transition from equilibrium of pressure to equilibrium of flow. The width of this region is equal to the length of the mean free path of the gas.

The radiometer forces are therefore ascribed to the edge of the vane rather than its surface. Maxwell (loc. cit.) had previously suggested that this might be the case. Einstein concludes that forces of this type are represented by the equation

$$F = p\Lambda \frac{\Delta T}{T}, \tag{402}$$

where F is the force per unit length of edge, p the pressure, Λ the mean free path and ΔT the difference in temperature between the two sides of the vane. This equation can only account for positive radiometer forces. Since Λ is inversely proportional to the pressure it would seem that equation (402) is in contradiction with the experimental results in that it predicts independence of F and p. Marsh,[1] however, has shown that ΔT is inversely proportional to the pressure. He also demonstrated that the effect is determined by the edges rather than by the surface of the vane. This has also been done independently by I. Bleibaum.[2] She also showed that if Smoluchowski's equation for the abrupt temperature change at a surface (cf. p. 195)

$$\Delta T = A\Lambda \frac{\partial T}{\partial x}, \tag{403}$$

where A is a constant, be inserted in equation (402) the resulting relation is

$$F = \frac{Ap\Lambda^2}{T} \frac{dT}{dx}. \tag{404}$$

This equation has been thoroughly tested by Brüche and Littwin,[3] using an apparatus in which the temperature gradient could be carefully controlled. They verified the predictions of equation (404) in that they found the force at high pressures to be proportional to the square of the mean free path, inversely proportional to the pressure and dependent upon the edge of the vane and not its surface.

Hettner [4] has derived equation (404) from assumptions at first sight entirely different from those of Einstein. Hettner believes that radiometer forces are

[1] H. Marsh, E. Condon and L. Loeb, *J. Opt. Soc. Am.*, **11**, 257 (1925); H. Marsh, *ibid.*, **12**, 135 (1926).

[2] I. Bleibaum, *Z. Physik*, **49**, 590 (1928).

[3] E. Brüche and W. Littwin, *Z. Physik*, **52**, 318, 334 (1928). Cf. also P. Schmudde, *ibid.*, **53**, 331 (1929).

[4] G. Hettner, *Z. Physik*, **27**, 12 (1924); *Exacte Naturwissenschaften*, **7**, 209 (1928).

caused by temperature gradients tangential to the surface rather than normal to it. He points out that if such a gradient exists along a surface in contact with a gas, the gas is set in motion (thermal flow, formula (386)). The radiometer forces are due to the reaction of this flow of gas. This had previously been suggested by Reynolds, as pointed out above, but the latter failed to carry the idea to its quantitative conclusion. Czerny and Hettner (loc. cit.) have shown the calculated forces to be present when a tangential temperature gradient is maintained in the radiometer vane. Hettner speaks of the phenomenon as a " thermal slip." He states that the edges of the vane and any points or projections will be at a lower temperature than the rest of the vane due to their better thermal conductivity. A flow of gas is then set up from the cold to the hot regions and the vane is set in motion by the reaction of this flow. This will explain the negative effect qualitatively for vanes, since in setting up a delicate vane it is difficult to avoid crumpling it slightly. See Fig. 28. These ideas are borne out by the fact that discrepancies indicating the presence of negative forces are found in the experimental results unless precautions are taken to insure that the vane be plane.

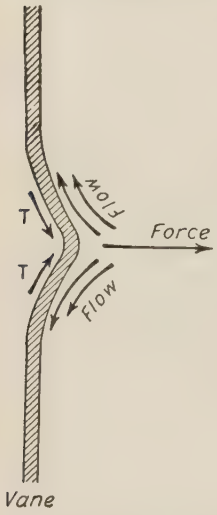

FIG. 28.

Hettner has applied his ideas to the various designs of radiometers. In all cases he considers the problem to be hydrodynamic in nature. Sexl [1] has given a more elaborate deduction of equation (404). His final equation contains a numerical factor dependent on the complexity of the gas molecule.

Miss Bleibaum (loc. cit.) has objected to the employment of the thermal slip in the explanation of radiometric forces at pressures of the order 10^{-2} mm. Hg. in that she considers the setting up of a flow unlikely at such low pressures. Hettner, however, regards his thermal slip and Einstein's edge effect to be different descriptions of the same phenomenon. Since they lead to the same equation, the experimental data cannot decide between the two.

The discussion has so far been confined to regions of high or low pressures. In the former case the force varies as $1/p$; in the latter with p. Hettner [2] and Brüche and Littwin (loc. cit.) have investigated the region of intermediate pressures where the mean free path of the gas is the same order of magnitude as the dimensions of the body experiencing the radiometric force. They assume that in this case the reciprocal of the total force is made up of two parts; one of which is inversely proportional to the pressure (Knudsen) and the other directly proportional to the pressure (Hettner's thermal slip or Einstein's edge effect). The total force is then given by

[1] T. Sexl, *Z. Physik*, **52**, 249 (1928).
[2] G. Hettner, *Z. Physik*, **37**, 179 (1926); **47**, 499 (1928).

$$\frac{1}{F} = \frac{a}{p} + \frac{p}{b}, \tag{405}$$

where a and b are constants depending on the design of the radiometer, the temperature and the nature of the gas. The first term is the Knudsen force, the second the Einstein-Hettner force. Hettner showed that the measurements of photophoresis carried out by Mattauch [1] are in excellent agreement with equation (405) and that the results obtained with the ordinary radiometer are in qualitative agreement with the relation. Brüche and Littwin obtain a quantitative agreement between the latter type of data and equation (405) since their data could be referred to a constant temperature gradient. They evaluate the constants of equation (405) from the experimental facts, found by them to the effect that the pressure at which the maximum force is found and the magnitude of this force are both proportional to the mean free path of the gas at some standard pressure.

Diffusion: When the kinetic theory was first proposed it met with the objection that, if the molecules actually have velocities of several hundred meters per second, gases should spread almost instantaneously, whereas it was well known that if hydrogen sulphide is set free in one corner of a room, several minutes elapse before it can be smelled in the opposite corner. This criticism was soon answered by Clausius who pointed out that the molecules of the foreign gas cannot move in a straight line from one corner of the room to the other but that, on the contrary, as a result of collisions with the air molecules already in the room, they move in a zig-zag path: their actual path from one point to another is incomparably greater than the rectilinear distance between the two points, provided this distance is large in comparison to the mean free path. If the space were evacuated until the mean free path was large in comparison to the distance between the two points, a very rapid spreading of the gas would actually take place, in fact, it would distribute itself with its thermal velocity.

This slow interpenetration of the molecules of two different gases is called diffusion. For a long time the theory of the phenomenon has been presented in contradictory ways. The simplest case which can be calculated accurately is one in which certain molecules of a gas are supposed to be recognizable from the others (Einstein speaks of them in his lectures as being " colored red "). These marked molecules are identical with the unmarked in respect to mass and diameter. The problem is now to follow their motion. (Maxwell's diffusion of a gas " into itself "). The diffusion of two isotopes into each other would illustrate the present situation approximately. The number of marked molecules passing from left to right through unit cross section per second is

$$\frac{|\overline{w}|}{6} N_A c' -, \tag{406}$$

[1] I. Mattauch. *Ann. Physik*, **85**, 967 (1928).

where $N_A c'_-$ is the number of marked molecules per cubic centimeter at a distance Λ from the area under consideration, or

$$N_A c'_- = \left(c' - \Lambda \frac{\partial c'}{\partial x} \right) N_A. \tag{407}$$

Similarly the flow from right to left is

$$N_A \frac{|\overline{w}|}{6} \left(c' + \Lambda \frac{\partial c'}{\partial x} \right) \tag{408}$$

and the net flow through unit area in unit time from right to left is

$$N_A \frac{|\overline{w}|}{3} \Lambda \frac{\partial c'}{\partial x}. \tag{409}$$

The same number of unmarked molecules passes through the same area in the opposite direction, the number being

$$- \frac{|\overline{w}|}{3} \Lambda \frac{\partial c}{\partial x} N_A. \tag{410}$$

Since, as a result of the equality of pressure throughout, the total density is everywhere the same,

$$c + c' = \text{constant}, \tag{411}$$

so that

$$- \frac{\partial c}{\partial x} = \frac{\partial c'}{\partial x}. \tag{412}$$

These two numbers are equal and the diffusion does not change the total pressure.

The diffusion constant D is defined from the relation giving the number of molecules diffusing through unit cross section in unit time, which is

$$D \frac{\partial c}{\partial x} N_A. \tag{413}$$

Therefore

$$D = \frac{|\overline{w}|}{3} \Lambda = \frac{|\overline{w}|}{3 N_A (c + c') \pi d^2 \sqrt{2}} \tag{414}$$

or

$$D = \frac{\eta}{M(c + c')} \tag{415}$$

A more exact calculation shows that the last expression must be multiplied by a numerical factor. D is seen to be inversely proportional to the total concentration.

If the marked molecules are different from the others, the values for $|\overline{w}|$ and Λ for each molecular species must be distinguished by marking one set with

primes. There is then obtained for the number of molecules of the first kind diffusing to the left

$$\frac{|\overline{w}'|}{3}\Lambda'\frac{\partial c'}{\partial x}N_A \tag{416}$$

and for the number of molecules of the second kind diffusing to the right:

$$-\frac{|\overline{w}|}{3}\Lambda\frac{\partial c}{\partial x}N_A. \tag{417}$$

The mean free path is given by equation (145), p. 81:

$$\Lambda' = \frac{1}{\pi N_A\left[d'^2\sqrt{2}c' + \left(\frac{d+d'}{2}\right)^2 c\sqrt{\frac{m+m'}{m}}\right]}, \tag{418}$$

$$\Lambda = \frac{1}{\pi N_A\left[d^2\sqrt{2}c + \left(\frac{d+d'}{2}\right)^2 c'\sqrt{\frac{m+m'}{m'}}\right]}. \tag{419}$$

The two currents of gas are in general of different amount so that an excess flow from right to left of magnitude

$$N_A\left(\frac{|\overline{w}'|\Lambda'}{3} - \frac{|\overline{w}|\Lambda}{3}\right)\frac{\partial c'}{\partial x} \tag{420}$$

is set up. As before, this is obtained from the fact that

$$\frac{\partial c'}{\partial x} = -\frac{\partial c}{\partial x}\ (c' + c = \text{const.}). \tag{421}$$

This effect would soon disturb the initial condition of equality of total pressure if the process took place in a closed tube. O. E. Meyer [1] assumes, therefore, that, in order to preserve the constancy of pressure, there is superimposed upon the calculated process a flow of the gas as a whole from left to right which just compensates the flow given by (420). Since the gas at the point under consideration is made up of a fraction $c'/(c + c')$ of molecules of the first kind and a fraction $c/(c + c')$ of molecules of the second kind, the equalizing flow from left to right of molecules of the first species equals

$$N_A\left(\frac{|\overline{w}'|\Lambda'}{3} - \frac{|\overline{w}|\Lambda}{3}\right)\frac{c'}{c+c'}\frac{\partial c'}{\partial x} \tag{422}$$

Similarly the corresponding flow of molecules of the second species, from left to right is

[1] O. E. Meyer, Kinetische Theorie der Gase, 1st ed., Breslau, 1877. For a criticism of this and other approximate theories see S. Chapman, *Phil. Mag.*, [7] 5, 630 (1928).

$$N_A\left(\frac{|\overline{w}'|\Lambda'}{3}-\frac{|\overline{w}|\Lambda}{3}\right)\frac{c}{c+c'}\frac{\partial c'}{\partial x}. \tag{423}$$

The total flow through unit cross section in unit time from right to left is therefore

$$\left.\begin{aligned} N_A\frac{|\overline{w}'|\Lambda'}{3}\frac{\partial c'}{\partial x}-N_A\left(\frac{|\overline{w}'|\Lambda'}{3}-\frac{|\overline{w}|\Lambda}{3}\right)\frac{c'}{c+c'}\frac{\partial c'}{\partial x} \\ =N_A\left[\frac{|\overline{w}'|\Lambda'}{3}\frac{c}{c+c'}+\frac{|\overline{w}|\Lambda}{3}\frac{c'}{c+c'}\right]\frac{\partial c'}{\partial x}. \end{aligned}\right\} \tag{424}$$

molecules of the first kind and from left to right

$$\left.\begin{aligned} N_A\frac{|\overline{w}|\Lambda}{3}\frac{\partial c'}{\partial x}+N_A\left(\frac{|\overline{w}'|\Lambda'}{3}-\frac{|\overline{w}|\Lambda}{3}\right)\frac{c}{c+c'}\frac{\partial c'}{\partial x} \\ =N_A\left[\frac{|\overline{w}'|\Lambda'}{3}\frac{c}{c+c'}+\frac{|\overline{w}|\Lambda}{3}\frac{c'}{c+c'}\right]\frac{\partial c'}{\partial x} \end{aligned}\right\} \tag{425}$$

molecules of the second kind. The diffusion coefficients of the two kinds have become equal, as must be the case if there is to be no onesided flow,

$$D'=D=\frac{|\overline{w}'|\Lambda'}{3}\frac{c}{c+c'}+\frac{|\overline{w}|\Lambda}{3}\frac{c'}{c+c'}. \tag{426}$$

However, they depend on the ratio of the concentrations c'/c and change from place to place of the diffusing columns.[1]

Gross [2] believed that the back flow could be neglected in the case of open tubes, retaining formulas (409) and (410). There is then also obtained a dependence upon the ratio of concentrations but it is not as pronounced as in Meyer's development and is of the opposite sign (i.e. according to one formula D should increase with increasing c', according to the other it should decrease but to a less extent). The experimental side of the problem was not settled for a long time. It was only known that the dependence was not as great as that required by (426) but whether or not it was present in general was not decided. A series of very careful experiments have shown (in the case of mixtures of H_2-O_2, N_2-H_2, O_2-N_2, H_2-CO_2, $Ar-He$) that there is a slight dependence, the direction of which is correctly given by O. E. Meyer's equation, but which is much smaller than that calculated. For example, in a 50 percent $Ar-He$ mixture D was found to be 0.25405, calculated 0.2537; for Ar/He = 0.377, found 0.25040, calculated, 0.208. Gross' formula gives the order of magnitude about correctly.[3]

[1] Cf. J. H. Jeans, The Dynamical Theory of Gases, 4th ed., Cambridge Univ. Press, (1925), Chapter XIII.

[2] G. Gross, *Wied. Ann.*, **40**, 424 (1890).

[3] Summarized by A. Lonius, *Ann. Physik*, **29**, 664 (1909).

In contrast to these equations Stefan [1] has deduced formulas according to which D does not depend on the ratio of the concentrations. His results, however, are not obtained from a purely molecular theory. It is postulated that the one gas moves to the right with the velocity W' and the other to the left with the velocity W. The two masses of gas moving in opposite directions exert a force (resistance) upon each other, which is assumed to be proportional to the product of the densities and to the relative velocity

$$A_{12}c'c(W' - W). \tag{427}$$

This must be overcome by the pressure gradient.

$$-\frac{\partial p'}{\partial x} = \frac{\partial p}{\partial x} = A_{12}cc'(W' - W). \tag{428}$$

The equation of continuity which states that, at the stationary state, just as much gas enters any element of volume as leaves it, here takes the form

$$c'W' = \text{constant}; \qquad cW = \text{constant} \tag{429}$$

and since there is no flow of the gas as a whole,

$$c'W' + cW = 0. \tag{430}$$

There follows further from the equality of the pressure that

$$p + p' = RT(c + c') = RTc_0, \tag{431}$$

whence

$$\left.\begin{aligned} -RT\frac{\partial c'}{\partial x} = RT\frac{\partial c}{\partial x} &= A_{12}[c'W'c - cWc'] \\ &= A_{12}[(c'W')(c_0 - c') - (cW)c'] \end{aligned}\right\} \tag{432}$$

or

$$-\frac{\partial c'}{\partial x} = \frac{\partial c}{\partial x} = \frac{A_{12}}{RT}[c'W'c_0 - (c'W' + cW)c'] = \frac{A_{12}}{RT}c'W'c_0. \tag{433}$$

The amount passing through unit area in unit time is then

$$c'W' = \frac{-RT}{A_{12}c_0}\frac{\partial c'}{\partial x}, \tag{434}$$

which is equal to

$$-cW = \frac{RT}{A_{12}c_0}\frac{\partial c}{\partial x}. \tag{435}$$

The common coefficient of diffusion is $D = RT/c_0A_{12}$ and is seen to be independent of the ratio of the concentrations.

Maxwell [2] has deduced the foregoing formula for D using his method for

[1] J. Stefan, *Wien. Ber.*, **65**, 323 (1872); Clerk Maxwell, *Phil. Mag.*, (4) **35**, 129 (1868).
[2] Clerk Maxwell, *Phil. Mag.*, **35**, 185 (1868); *Scient. Papers*, **2**, 61, 501.

molecules repelling each other with an inverse fifth power law; and Boltzmann [1] has found, after a lengthy calculation, that the diffusion coefficient for elastic spheres is independent of the ratio of concentrations. More recently Langevin [2] has also stated this independence. Finally the rigorous method of Enskog (p. 136) shows the diffusion coefficient to be

$$D = \frac{3\sqrt{RT}}{32\sqrt{2\pi}N_A\Psi}\sqrt{\frac{M+M'}{MM'}}\frac{1}{c+c'}, \tag{436}$$

where Ψ depends upon the law of force between the molecules and for the case of elastic spheres equals $(d + d')^2/16$.

This formula, which requires that D be independent of the ratio of concentrations, is only a first approximation. The second approximation introduces on the right hand side the factor

$$1 + \frac{A_{II}\left(1+\beta_{II}\frac{c}{c'}\right) + A'_{II}\left(1+\beta'_{II}\frac{c'}{c}\right) - 52A_{II}A'_{II}}{\left(1+\beta_{II}\frac{c}{c'}\right)\left(1+\beta'_{II}\frac{c'}{c}\right) - 676\,A_{II}\,A'_{II}}, \tag{437}$$

where

$$\beta_{II} = \left(\frac{2d}{d+d'}\right)^2\sqrt{\frac{m+m'}{2m'}}\frac{4(m+m')^2}{15m^2+8mm'+6m'^2}, \tag{438}$$

$$\beta'_{II} = \left(\frac{2d'}{d+d'}\right)^2\sqrt{\frac{m+m'}{2m}}\frac{4(m+m')^2}{6m^2+8mm'+15m'^2}, \tag{439}$$

$$A_{II} = \frac{m'^2}{12m^2+16mm'+30m'^2}, \tag{440}$$

$$A'_{II} = \frac{m^2}{30m^2+16mm'+12m'^2}. \tag{441}$$

The experimental results are well represented by this equation. Enskog gives the following figures:

The diffusion constant of a mixture of gases 1 and 2 in the ratio three to one ($D_{(3/1)}$) is compared with the diffusion constant in a mixture in which the ratio is one to three, ($D_{(1/3)}$). Then

Gas 1 Gas 2	Ar He	O_2 H_2	CO_2 H_2
$\frac{D_{(3/1)}}{D_{(1/3)}}$ (exp.)	1.11	1.048	1.067
$\frac{D_{(3/1)}}{D_{(1/3)}}$ (theor.)	1.072	1.076	1.078

Cf. also: S. Rosseland, *Physica*, **5**, 381 (1925).

[1] L. Boltzmann, *Wien. Ber.*, **86**, 63 (1882); **88**, 835 (1883); *Ges. Abh.*, **3**, 3, 63.

[2] P. Langevin, *Ann. chim. phys.*, **5**, 245 (1905).

It has further been found by Enskog and by Chapman [1] (loc. cit.) that if a temperature gradient is suddenly applied to a homogeneous mixture of gases, diffusion takes place. In the case of elastic molecules (in general in the case of molecules which repel each other with a law of force in which the exponent is less than -5) the heavier gas moves in the direction of the gradient. The gradient of the partial pressure at the stationary state is given by

$$\frac{dp}{dx} = -\frac{dp'}{dx} = \tilde{D}\frac{dT}{dx}, \tag{442}$$

where

$$\tilde{D} = k\frac{c\beta_{III} - c'\beta'_{III}}{\left(1 + \beta_I\frac{c'}{c}\right)\left(1 + \beta'_I\frac{c}{c'}\right) - \frac{A_I^2}{4\lambda\lambda'}}, \tag{443}$$

(for the magnitudes β_I, β'_I, A_I, see p. 199.)

$$\beta_{III} = \frac{5}{8}\frac{(d+d')^4}{(4dd')^2}\frac{\sqrt{mm'}}{m+m'}\left[\frac{4d^2}{(d+d')^2}\frac{m\sqrt{2}}{\sqrt{(m+m')m'}} - \frac{m'(15m' - 7m)}{2(m+m')^2}\right]. \tag{444}$$

The equation for β'_{III} is obtained by exchanging the primed and unprimed quantities. Dootson and others [2] have given experimental demonstrations of this effect (thermal diffusion).

Theory of the Diffusion Pump: [3] Consider a gas contained in a horizontal tube. The symbols referring to this gas will be designated by primes in the following discussion. Through this first gas a second diffuses from right to left. The properties of the second gas will be designated by two primes. The number of molecules of the second gas diffusing through unit area in unit time is

$$-D\frac{dc''}{dx}. \tag{445}$$

Assume that the first gas is moving to the right with a velocity W. Then the quantity of the second gas flowing to the right is $c''W$ if no diffusion takes place and if both gases move together. Taking both effects into account the total flow of the second gas to the right is

$$c''W + D\frac{dc''}{dx}, \tag{446}$$

[1] S. Chapman, *Phil. Mag.*, **34**, 146 (1917).

[2] S. Chapman and F. W. Dootson, *Phil. Mag.*, **33**, 248 (1917); T. Ibbs, *Proc. Roy. Soc.*, **99A**, 385 (1921); *ibid.*, **107A**, 470 (1925); G. Elliott and D. Masson, *ibid.*, **108A**, 378 (1925); T. Ibbs and L. Underwood, *Proc. Phys. Soc.*, London, **39**, 227 (1927).

[3] W. Gaede, *Ann. Physik*, **46**, 357 (1915); *Z. f. techn. Physik*, **4**, 337 (1923). For the pumps designed by Langmuir and others see S. Dushman, High Vacuum Technique, Schenectady, 1922. In this paragraph the magnitude of the velocity $|W|$ will be written W.

and of the first

$$c'W + D\frac{dc'}{dx}. \tag{447}$$

Since

$$c' + c'' = \text{constant} = c_0 \tag{448}$$

the second expression becomes

$$c_0W - \left(c''W + D\frac{dc''}{dx}\right). \tag{449}$$

That is, the amount of the first gas flowing to the right equals the difference between the total amount flowing into the right and the amount of the second flowing to the right.

If a stationary state is assumed, equal amounts of each gas must flow through every cross section, whence

$$c''W + D\frac{dc''}{dx} = \text{constant} = B \tag{450}$$

or

$$c'' = \frac{B}{W} + \left(c_{x=0}'' - \frac{B}{W}\right)e^{-\frac{W}{D}x} \tag{451}$$

and if the concentration c_1'' prevails at the point x_1,

$$\frac{c''_1 - c''_0 e^{-\frac{W}{D}x_1}}{1 - e^{-\frac{W}{D}x_1}}W = B. \tag{452}$$

In the integration of equation (450) it is assumed that W and D are independent of x, which may or may not be justificable according to the conditions of the flow.

If the diffusion of the second gas to the left is just compensated by its flow to the right $B = 0$ and

$$W = \frac{D}{x_1} ln \frac{c''_0}{c''_1}. \tag{453}$$

The diffusion pump depends upon the principle discussed here, namely, that the diffusion of a gas caused by its own partial pressure gradient also takes place against the flow of another gas, if the latter is not too rapid. Consider two spaces A and B connected by means of a narrow tube. B is connected to the receiver to be evacuated and is therefore full of the gas which is to be pumped away (designated with the double prime). In A there is boiling mercury. The partial pressure of the gas to be pumped out is maintained lower in A than in B by the rapid stream of mercury vapor flowing past the mouth of the connecting tube. This stream entrains and carries away all

the gas which diffuses through the tube. Of course the mercury vapor streams through the tube into B but, on account of the small diameter of the tube, this is not sufficiently rapid to prevent the diffusion in the reverse direction of the gas which is being removed. The partial pressure of the mercury vapor is maintained at a low value in B by continuous water cooling.

The pressures in common practice fall in the region intermediate between diffusion proper and Knudsen's effusion (p. 164). Gaede (loc. cit.) has carried out some calculations for the latter extreme case.[1]

Equation (453) may also be written

$$c''_1 = c''_0 e^{-\frac{Wx_1}{D}}, \tag{454}$$

giving the concentration of the second gas diffusing against a flow of the first as a function of the distance and velocity of flow. This principle has been applied to the separation of gaseous mixtures, since the different constituents of the mixture diffuse at different rates into the flowing gas (due to their differing diffusion coefficients) and therefore a partial separation is effected.[2]

[1] For a more detailed theoretical discussion, together with some experimental work see W. Molthan, *Z. techn. Physik*, **7**, 377, 452, (1926). Cf. also for description of various diffusion pumps: S. Dushman, Production and Measurement of High Vacuum, Schenectady (1922); L. Dunoyer, Vacuum Practice, trans. by J. H. Smith, D. Van Nostrand and Co., 1928.

[2] G. Hertz, *Physik. Z.*, **23**, 433 (1922); R. Wussow, Brennstoff-Chemie, **5**, 65 (1924).

CHAPTER IV

IMPERFECT GASES AND THE LIQUID STATE

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An ideal or perfect gas was defined in Chapter II as a gas whose internal energy is independent of the volume and which obeys the equation of state

$$pV = \text{constant.} \tag{455}$$

It has been shown in the previous chapter that an assemblage of molecules fulfills these conditions if it is so attenuated that the volume of the molecules themselves is small in comparison with the total volume and if the forces between the molecules are negligible except during collisions. Experiment shows, however, that as the concentration of the gas is increased the equation of state (455) no longer expresses the behavior of the gas. When this is the case the gas is said to be " imperfect." The present section will be devoted to a description of the changes which must be made in the treatment of the problems of the gaseous state when the simplifying assumption of a dilute or perfect gas can no longer be made.

Derivation of the van der Waals Volume Correction: In the foregoing deduction of the pressure equation (pp. 75–78) the molecules were treated as dimensionless points. In order to introduce the effect of their finite size the simple case of a single molecule moving back and forth perpendicular to the walls of the rectangular container will again be considered. The amount of momentum transferred to the wall is, as before, $2m\xi$ per collision. The frequency of collisions, however, is increased since the center of the molecule cannot get closer to the wall than the length of its radius, $d/2$. On going from one wall to the other, therefore, the center of the molecule only traverses the distance $l_1 - (2d/2)$, and requires a correspondingly shorter time. It collides more frequently than before in the ratio

$$\frac{l_1}{l_1 - d} = \frac{1}{1 - d/l_1} \tag{456}$$

and the pressure is increased by the same proportion.

The essential parts of this argument are not changed upon passing from this imaginary case to that of an actual gas. The effect of an individual collision at a given temperature and hence at a given kinetic energy is still the same as in the case of an ideal gas, but the number of collisions with the wall

per unit of time in the present case is greater than before due to collisions among the molecules. For example, consider a molecule moving parallel to the X-axis with velocity ξ. If such a molecule collides head on with a second molecule moving in exactly the opposite direction, their velocities are exchanged and the second molecule moves on toward the wall instead of the first one. At the moment of the collision, however, the second molecule was nearer to the wall than the first and therefore does not have to go as far to collide with the wall as would the first, had there been no collision between the molecules. The transported momentum has jumped over a portion of its path equal in length to the molecular diameter. In this interval it is carried not by the motion of the molecule but by whatever processes exchange the velocities of the colliding molecules. If the molecules were perfectly elastic spheres these would be elastic waves. In real molecules, however, they are electrical processes and electron motions in the interior of the atoms.

The ratio of the time required to transport the momentum through the distance d by collision to the time necessary for its transport through the same distance without collision (by means of the motion of the molecule) is therefore equal to the ratio of the molecular velocity to the velocity of the elastic wave or electrical reaction within the atoms. This is vanishingly small so that in the further calculations it may be assumed that at each collision the momentum is instantaneously carried through a definite interval. In other words, the quantity

$$\frac{\text{time in which the molecules are in contact}}{\frac{d}{w}}$$

is to be neglected. At normal temperatures and pressures d/w is of the order of 2×10^{-12} sec. Nothing definite is known about the time during which the molecules are actually in contact during a collision.

If all collisions were head on, each collision would save a distance d; if the number of collisions per cm. were N', the saving would be $N'ld$ and, accordingly, the number of collisions and the pressure increased by the factor

$$\frac{l}{l - N'ld} = \frac{1}{1 - N'd}. \tag{457}$$

This has to be modified somewhat, because not all the collisions are head on. The average shortening of the path is equal to the average value of all the parallels laid transversely through a sphere of radius $d/2$, since each element of area of the sphere is hit equally often.[1] In other words, at each

[1] If two molecules collide in such a manner that the line of centers makes an angle ϑ with the relative velocity, the shortening of the path is $d \cos \vartheta$. The number of such collisions is proportional to $\sin \vartheta d\vartheta$ and the average shortening of the path is therefore

$$d \int_0^{\pi/2} \cos \vartheta \sin \vartheta d\vartheta = \frac{d}{2}.$$

collision the momentum jumps over an interval of length equal to the chord drawn from the point of contact parallel to the direction under consideration, thus for the X-component of momentum the chord is drawn parallel to the X-axis. The average decrease in the length of the path is therefore found to be

$$d/2. \tag{458}$$

The relative change of the number of collisions against the wall is then, on the average,[1]

$$\frac{\Lambda}{\Lambda - \frac{d}{2}} = \frac{1}{1 - \frac{d}{2\Lambda}}. \tag{457'}$$

Upon substituting the value of the mean free path,

$$\Lambda = \frac{3}{4\pi \frac{N_A}{V} . d^2} \tag{459}$$

(where V is the mol volume), there is obtained, after simplification, the increase of the pressure

$$\frac{1}{1 - \frac{b}{V}}, \tag{460}$$

where

$$b = \frac{4\pi}{3} \frac{N_A d^3}{2} = 4N_A \frac{4\pi}{3} \left(\frac{d}{2}\right)^3. \tag{461}$$

b is therefore four times the true volume of the molecules contained in one mol. The equation of state becomes

$$pV = RT \frac{1}{1 - \frac{b}{V}} \qquad \text{or} \qquad p(V - b) = RT. \tag{462}$$

This formula, however, is only valid when b is small in comparison with V. Thus in order that $V = b$ the formula requires an infinitely high pressure, so that $V = b$ would be the smallest possible volume. Actually, however, the closest possible packing of a number of spheres is that arrangement in

[1] This deduction is not rigorous. Actually, the diminution of the mean free path is given by

$$\frac{1}{1 + \frac{5}{8}\frac{b}{V}} \text{ (Clausius).}$$

But the inexactitude incurred by the choice of the expression for the shortening of the mean free path is compensated by an inaccuracy in the mean free path. The result, therefore, is correct as will be shown shortly by a more rigorous method. (Cf. p. 223.)

which the centers of all the spheres lying in one plane are on the vertices of equilateral triangles and the spheres in the planes immediately above and below fill up the gaps between the spheres of the first plane. Then the centers of any four adjacent spheres form a tetrahedron of side $2r$ and volume $(2/3)\sqrt{2}r^3$ (tetrahedral packing). Each of these tetrahedra includes one sixth of a sphere. Therefore N_A spheres of total volume $N_A(4/3)\pi r^3 = b/4$, will occupy a space of about $b/3$. The reason that the correction is smaller at the smaller volumes is that those collisions in which the momentum makes the longest jump, i.e., head-on collisions, occur relatively less frequently. This becomes evident on considering a tetrahedral packing in which the spheres can only move slightly.

The more exact consideration of the effect of close packing has been the subject of many researches. It must be pointed out, however, that in such exact calculations it is no longer permissible to regard the molecules as elastic spheres.

The transportation of momentum by jumps may be treated in another manner which will be useful later on since it is valid at especially high densities.[1] Consider a plane placed in the gas. If this plane were a material, impenetrable wall of infinite thinness it would be subjected on both sides to the pressure of the gas.[2] The magnitude of this pressure on one side of the wall say, for example, the left, equals the amount of momentum which would be transported from left to right through the plane of the wall in unit time per unit area, multiplied by two to take into account the reflection of the molecules from the wall (cf. p. 76). This transport of momentum may be classified under two heads according to the mechanism of transport. In the first place molecules moving from the left hand side of the plane to the right will contribute to the total transport of momentum. A process by which momentum is transported by this first means will be defined as one in which the center of the transporting molecule actually passes *through* the plane. The second method by which momentum may be conveyed though the plane consists in " jumps " of momentum due to collisions. A process of the second kind will be defined as one in which the centers of the transporting molecules do not pass through the plane (Fig. 29).

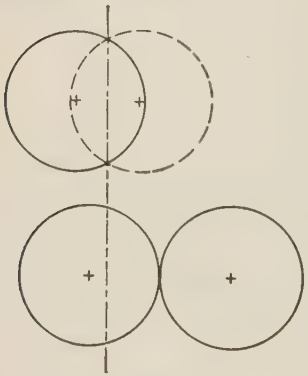

Fig. 29

[1] G. Jäger, *Wien. Ber.*, **105**, 15 (1896); *Z. physik. Chem.*, **93**, 289 (1919); L. Boltzmann, *Wien. Ber.*, **105**, 695 (1896). For further references see *Enz. d. Math. Wiss.*, Vol. **8**, 552.

[2] The pressure exerted on a wall is, in general, equal to the thermal pressure minus the cohesion pressure caused by the attractive forces of the molecules (cf. p. 225). This cohesion pressure, however, would not come into account in the case of an infinitely thin wall both sides of which are in contact with the fluid, since the attractions of the molecules on the two sides neutralize each other. In this case the thermal pressure alone remains to be considered.

It is now to be shown that the pressure due to momentum transported by the first type of process always equals RT/V as in the case of a perfect gas. Let it be assumed that the mean free path Λ is very small, that is, of the order of the molecular dimensions. Then, to return again to the former approximation in which 1/3 of all the molecules are supposed to be moving either from left to right or in the reverse direction, it is seen that only those molecules which are not farther than Λ from the plane can move so that their centers pass through it. The number of such molecules per unit area of the plane is $N_A\Lambda/3V$. According to this simplified model all of these molecules will move from left to right a distance Λ and will then return from right to left the same distance. Each molecule, therefore, passes through the plane from left to right $\xi/2\Lambda$ times per second. The total number of molecules whose centers pass through unit area of the plane in unit time is therefore

$$\frac{N_A\Lambda}{3V} \cdot \frac{\xi}{2\Lambda} = \frac{N_A\xi}{6V}, \tag{463}$$

which is independent of the magnitude of the mean free path. The pressure exerted by these molecules is

$$2\,\frac{N_Am\xi^2}{6V} = \frac{RT}{V}. \tag{464}$$

The remaining part of the thermal pressure is due to the transport of momentum by the second type of process, that is, by the "jumping" of momentum through these molecules, which penetrate the plane but whose centers do not pass through it. At moderately low densities this part of the pressure amounts to $(RT/V - b) - (RT/V)$ as was deduced above. There is no well founded general theory of the change in this quantity at high densities.[1] For very dense gases and for liquids, however, the thermal pressure increases very rapidly with further decrease of volume. If the molecules, when close together, could be regarded as elastic spheres, the thermal pressure at constant volume would always be proportional to the absolute temperature.[2]

Another method of determining the volume correction consists in calculating the geometric mean of the free volume available for each molecule. In order to calculate this quantity, consider an empty volume V, into which N_A molecules are put one at a time. The volume available after each addition is calculated and the product of these N_A terms is found. The N_Ath root of this product is the desired mean.

The first molecule has the whole volume V available, apart from a negligibly thin skin along the walls. Assume that a sphere of radius $2r$ is circumscribed around the molecule (p. 119) so that the center of no other molecule can penetrate this sphere. Let the volume of this sphere equal $b' = \frac{4\pi}{3}(2r)^3$.

[1] E.g., R. Becker, *Z. Physik*, **4**, 393 (1921).
[2] R. Clausius, *Pogg. Ann.*, **100**, 358 (1857).

Then the center of the second molecule has available the whole volume V minus the space filled by the sphere around the first. Thus the volume available for the second molecule is $V - b'$. The third molecule has available the whole volume minus the space filled by the two protecting spheres, i.e. $V - 2b'$. This procedure neglects the possibility that the two spheres of the first two molecules might occasionally overlap. In this case the forbidden space would be less than $2b'$. In neglecting the overlapping (which amounts to neglecting the simultaneous interaction of three, or later on more, molecules) the deduction is restricted to the first order in the volume correction. Proceeding in the same manner, the space available for the last (N_Ath) molecule is found to be $V - (N_A - 1)b'$.

The product of all these volumes is then [1]

$$\prod_{s=0}^{s=N_A-1} (V - sb'). \tag{465}$$

To calculate the N_Ath root of this, take the logarithm and divide by N_A

$$\frac{1}{N_A} ln\ \Pi(V - sb') = \frac{1}{N_A}[\textstyle\sum^s ln(V - sb')]; \tag{466}$$

the logarithms are next developed to the first power in b'/V:

$$\left.\begin{aligned} \frac{1}{N_A}\textstyle\sum^s ln(V - sb') &= \frac{1}{N_A}\sum_0^{N_A-1}{}^s \left[lnV + ln\left(1 - \frac{sb'}{V}\right)\right] \\ &= lnV + \frac{1}{N_A}\sum_0^{N_A-1}{}^s \left(\frac{sb'}{V}\right) = lnV - \frac{1}{N_A}\frac{b'}{V}\frac{N_A(N_A-1)}{2} \\ &= lnV - \frac{b'(N_A - 1)}{2V}. \end{aligned}\right\} \tag{467}$$

It is possible to substitute N_A for $N_A - 1$ without appreciable error. A quantity b is now defined by the equations

$$b = \frac{b'}{2}N_A = 4N_A\frac{4\pi}{3}r^3 \tag{468}$$

or 4 times the total volume actually occupied by molecules. With the same accuracy as before, it follows that

$$-\frac{b}{V} = ln\left(1 - \frac{b}{V}\right) \tag{469}$$

or

$$\frac{1}{N_A} ln\left[\Pi(V - sb')\right] = lnV + ln\left(1 - \frac{b}{V}\right) = ln(V - b). \tag{470}$$

[1] Cf. Note 2, p. 92.

To the first order correction, $V - b$ is therefore the mean free volume available to the molecules in one mol.

The statement might have been made that the volume occupied by all other spheres is $(N_A - 1)b'$, but then every molecule would have been counted while one half must be counted as points only, so that the true value is

$$b \sim \frac{(N_A - 1)b'}{2}.$$

The Van der Waals' Inner or Cohesion Pressure: It is evident that a consideration of the actual volume of the molecules is not sufficient to account for the differences between ideal gases and very dense gases or liquids, since in the latter the thermal pressure p_t has enormous values. That a liquid can exist at all at ordinary pressures must be due to the presence of attractive forces between the molecules. The action of these forces may be described by what is known as the internal cohesion pressure p_i, which must be subtracted from the thermal pressure to obtain the experimentally measured external pressure. In order to deduce the formula for p_i van der Waals resorted to the method used in the theory of capillarity. He assumed the presence of attractive forces with a range of action smaller than 1 cm. but still much larger than molecular dimensions.[1] The mutual action between two elements of volume is simply proportional to the numbers of molecules contained in them, or inversely proportional to the product of the mol volumes.

$$F \sim \frac{1}{V} \times \frac{1}{V} = \frac{\text{constant}}{V^2}.$$

The manner in which the force varies with the distance appears only in the constant, which is independent of the volume. Furthermore, since the molecules are distributed uniformly through space, on the average, a molecule in the interior of the fluid is uniformly surrounded by other molecules whose effects neutralize each other. Thus, there is an excess force only at the surface. The van der Waals' cohesion pressure is therefore

$$p_i = p_t - p = \frac{a}{V^2} \tag{471}$$

and can be considered as a pressure exerted by the surface layer, acting like the membrane in a toy balloon.

Since a measures the strength of the attractive forces which also cause the change of the mean free path with the temperature, there is a close connection between the van der Waals a and the Sutherland constant C (p. 128).

The above deduction, although yielding the correct result, is founded upon the incorrect assumption that the range of action of the molecular forces is

[1] This assumption is not necessary (cf. below). The actual range of action is about 3×10^{-8} cm.

large in comparison to the molecular diameter. The following procedure is not subject to this objection.[1]

Assume that each molecule is surrounded by a field of force such that two molecules r cm. apart possess a potential energy equal to $\epsilon(r)$. In an exact analysis this potential energy may depend on the mutual orientation of the molecules. If the forces are attractive, ϵ is negative. In order to deduce the equation of state appropriate to this assumption it will be necessary to calculate the increase in the internal energy of the gas due to the intermolecular forces. This will be accomplished by determining the frequency with which any definite value of the energy appears, multiplying this energy with the corresponding frequency and summing over all values of the energy. In order to simplify the calculation it will further be assumed that the range of action of the attractive forces is small and that the gas is so dilute that the potential energy due to two molecules an *average* distance apart is small in comparison to kT. Then each molecule may be supposed to be surrounded by a sphere of action such that an appreciable amount of potential energy is contributed to the total energy of the gas only if the center of another molecule is within the sphere of action of the first. The radius, r_a, of this sphere of action is therefore small in comparison to the average distance between the molecules. It is true that r_a is not sharply defined since, as kT decreases, potential energies at greater and greater distances become appreciable, but this turns out to be without influence on the calculations. The frequency with which the center of a given molecule appears in a given volume element dV is, in the absence of molecular forces, dV/V. In the presence of such forces the Boltzmann equation states that it is

$$dW = \frac{e^{-\frac{\epsilon(r)}{kT}} dV}{V - V_0 + \int e^{-\frac{\epsilon}{kT}} dV}, \tag{472}$$

where V_0 equals the total volume of the spheres of action $(N_A(4/3)\pi r_a^3)$, $V - V_0$ is therefore the free volume throughout which $\epsilon = 0$. The integral represents the sum of the weighted probabilities that the center of the given molecule should lie within an element dV in which the potential energy is ϵ. Since the gas under discussion is dilute the whole denominator may be set equal to V. Upon following the procedure outlined above, the average energy added to the internal energy of the gas by the molecular forces is found to be

$$\overline{U}_p = \frac{N_A^2}{V} \int \epsilon(r) e^{-\frac{\epsilon(r)}{kT}} dV. \tag{473}$$

The exponential term in this expression corresponds to the formation of " clusters " of molecules (association). If the temperature is sufficiently high

[1] Cf. W. H. Keesom, Comm. Leiden (1912–1914), No. 24*a*, *b*, 25, 26; (1915–1916) No. 39*a*, *b*, *c*. *Physik. Z.*, **22**, 129, 643 (1921); **23**, 225, (1922); P. Debye, *Physik. Z.*, **21**, 178 (1920).

this term may be set equal to unity ($\epsilon(r) \ll kT$). This approximation is equivalent to the statement that the center of a given molecule appears in an element of a sphere of action just as often as in an element of the free volume. The mean potential energy of the gas then becomes

$$\overline{U}_p = \frac{N_A^2}{V} \int \epsilon(r) dV. \tag{474}$$

The presence of V in the denominator of this expression means that as the volume increases the molecules spend less and less time in the spheres of action of other molecules. The nature of the molecular forces only influences the quantity $N_A^2 \int \epsilon dV$ which, in Van der Waals equation, is symbolized by a. At low temperatures, the exponential must be retained, that is, association must be taken into account. In general (473) may be expressed as a series, the equation then becoming

$$\overline{U}_p = \frac{N_A^2}{V}\left[\int \epsilon(r) dV - \frac{1}{kT}\int \epsilon^2 dV + \frac{1}{2(kT)^2}\int \epsilon^3 dV \ldots\right]. \tag{475}$$

At sufficiently high temperatures all terms but the first may be neglected.

Upon substitution of $\overline{U}_p$ in the thermodynamic equation of state [1]

$$p = T\left(\frac{\partial p}{\partial T}\right)_V - \left(\frac{\partial U}{\partial V}\right)_T. \tag{479}$$

van der Waals' equation appears in the familiar form

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT, \tag{480}$$

the integration constant being evaluated from the fact that, at sufficiently great volumes, the equation must reduce to equation (462).

Discussion of van der Waals' Equation: It must be emphasized at this point that the derivation of van der Waals' equation rests upon the assumption that the gas deviates but slightly from the ideal state. The equation is therefore only a first approximation to the expression of the behavior of imperfect gases. Hence, the quantitative application must be limited to

[1] Consider any substance carried through an infinitesimally small Carnot cycle. The work done is

$$p\Delta V - \left(p - \frac{\partial p}{\partial T}\Delta T\right)\Delta V. \tag{476}$$

This is also equal to

$$\frac{Q}{T}\Delta T \tag{477}$$

and, by the first law of thermodynamics,

$$Q = \frac{\partial U}{\partial V}\Delta V + p\Delta V. \tag{478}$$

On equating (476) and (477) and substituting from (478) equation (479) is obtained.

moderately concentrated gases. On the other hand it is to be expected that the equation may give a qualitative description of the behavior of condensed gases over a wide range. Since this is found to be the case, van der Waals' equation is usually employed as the starting point for a discussion of the relations between the gaseous and the liquid states.

Before proceeding to the physical content of van der Waals' equation it is desirable to deduce its analytical properties. For a given gas, that is, given values of a and b, the equation describes a surface in the three dimensional space of coordinates p, V and T. It is more convenient, however, to plot p as ordinate against V as abscissa for a number of constant values of T. Such curves are known as isothermals. In the case of a perfect gas they are the family of rectangular hyperbolas,

$$pV = \text{constant.} \tag{481}$$

If the gas is such that only the van der Waals volume correction need be taken into account, the equation of the isothermal is

$$p(V - b) = \text{constant.} \tag{482}$$

Their shape has not been altered by taking into account the finite volume of the molecules, the only change being to displace the whole family of curves b units to the right in the p-V plane.

If, however, both the pressure and the volume corrections are taken into account, not only the position of the family of isothermals but also their shape is altered. The equation

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \tag{483}$$

is of the third order in V, since it may be transformed to

$$V^3 - \left(b + \frac{RT}{p}\right)V^2 + \frac{a}{p}V - \frac{ab}{p} = 0. \tag{484}$$

For any set of values of the coefficients therefore there are three roots of the equation. These roots, however, need not all be real. In order to determine the form of the curves, the first and second derivatives of the equation may be written as follows:

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V - b)^2} + \frac{2a}{V^3}, \tag{485}$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{2RT}{(V - b)^3} - \frac{6a}{V^4}. \tag{486}$$

If the temperature is sufficiently high, the first term on the right of each of these equations will predominate. Since, in this case, the first derivative is negative and the second positive, the isothermals corresponding to high values of T

slope downward from left to right and are concave upward. In the equation

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT, \tag{480}$$

a/V^2 is then of little importance because, for small and moderate pressures, V is large, while for small V, p is very large. At lower temperatures the first term on the right of equation (485) no longer predominates throughout. Thus if V is only slightly greater than b, the first term on the right of equation (485) is very large; $\partial p/\partial V$ is large and negative. Hence, at the start, the curve shows a steep descent. As V becomes larger, however, $(V - b)^2$ increases more rapidly than V^3 so that $\partial p/\partial V$ goes through zero and becomes positive. In this region the curve has gone through a minimum. As V becomes large in comparison to b, V^3 increases more rapidly than $(V - b)^2$. The first derivative therefore again goes through zero and becomes negative. In this region the curve exhibits a maximum. These stationary points are given by

$$\frac{RT}{(V - b)^2} = \frac{2a}{V^3}. \tag{487}$$

This cubic equation has three roots, one of which is at infinity. The present discussion is concerned with the other two. As V increases further, $\partial p/\partial V$ tends toward zero. The curve, therefore, approaches the V-axis asymtotically. Fig. 30 shows a sketch of the curves obtained from van der Waals' equation. Curves I and II are typical of the high temperature region and, as T increases, the curves approach the rectangular hyperbola of a perfect gas. Curves IV and V are typical of the low temperature region. At pressures between the maximum and minimum shown by each of these curves there are three real roots (values of V for a given p) to the equation. At all other pressures there is only one real root, the other two being imaginary and hence without physical significance. It is evident from the figure that, as the temperature increases, the maximum and minimum come closer together. The boundary between what have been called the high and low temperature regions is formed by that curve in which the maximum and minimum coalesce to form a point of inflection, which is called the critical point (K, Fig. 30). At this point the three real roots of the curve coincide. The point may be determined by setting both $\partial p/\partial V$ and $\partial^2 p/\partial V^2$ equal to zero and solving for the corresponding volume, temperature and pressure in terms of a and b.

The physical significance of the curves of Fig. 30 will now be discussed. The curves of the high temperature region represent the behavior of compressed gases at least qualitatively. As the temperature increases the curves approach a rectangular hyperbola; van der Waals' equation approaches the perfect gas equation and the gas itself approaches the ideal state.

The interpretation of the low temperature region is not as obvious. Thus, throughout the interval of each curve included between the minimum and the maximum, $\partial p/\partial V$ is positive. This means that increasing the pressure on the

substance causes an *increase* in volume. Such behavior is contrary to all experience. Furthermore any such state would be highly unstable.[1] The anomaly is explained by the fact that van der Waals' equation describes a supposed homogeneous system, whereas in the interval under discussion part of the gas has condensed to a liquid and the system contains the two phases,

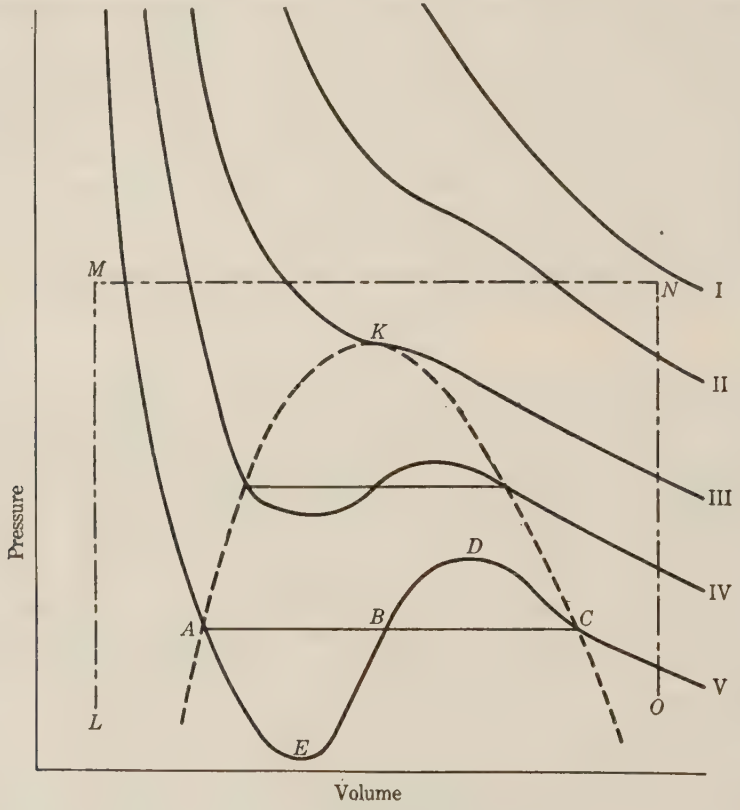

FIG. 30

liquid and vapor. It is known from experiment and from the thermodynamic treatment that, at a given temperature, a vapor in equilibrium with its liquid exerts a definite constant pressure, independent of the total volume (cf. also p. 245). The S-shaped part of van der Waals' curve *AEDC* (Fig. 30) is therefore replaced with the straight line *ABC*. The treatment of the parts *AE*, *DC* as unstable, but not impossible states, finds its justification in the fact that the pressures of supercooled vapors and superheated liquids follow the general path of the lines *CD* and *AE* respectively. It has been deduced [2]

[1] According to G. Bakker, (*Z. physik. Chem.* **104**, 10 (1922)), this state is realized in the surface layer separating the liquid from its vapor.

[2] J. C. Maxwell, Collected Works II, p. 425; Clausius, *Wied. Ann.*, **9**, 337 (1880).

thermodynamically that the exact position of the line *ABC*, representing the equilibrium between liquid and vapor, is such that the area *AEB* equals the area *BDC*. Such a procedure, however, presupposes too great an accuracy for van der Waals' equation in a region where it can be expected to agree only qualitatively with experiment.

The points on the straight line *ABC* represent two-phase-systems, the specific volumes of each phase being constant and represented by the end points *A* and *C* of the line. The intermediate points represent mixtures of liquid and vapor in varying amounts. Thus, the midpoint of the line is the state point of a mixture of equal parts of liquid and vapor. The transition from *A* to *C* corresponds to the evaporation of one mol of liquid at constant pressure and temperature. The dotted line of Fig. 30 is a locus of the end points of the line *ABC*. The right hand side of this curve gives the change of the equilibrium pressure and molar volume of the saturated vapor with varying temperature, going from one isotherm to another. The left hand part gives the change of (the same) pressure and the molar volume of the liquid with the temperature. A system whose statepoint is located in the area enclosed by this curve is composed of two phases; throughout the rest of the plane the statepoints represent one phase systems.

The isotherm from *C* on to the right is then the isotherm of the unsaturated (superheated) vapor, taking on more and more the form it has for an ideal gas. The curve to the left of *A* represents, at least for a certain distance, the relation between volume and pressure for the liquid, showing in its steepness the smaller compressibility of the liquid. It follows from the preceding discussion that the only definite difference between a gas and a liquid is the property of liquids of forming an independent surface, that is, one not determined by the wall of the container.

Other differences between gases and liquids are of degree and not fundamental. Unless this distinguishing property of independent surface is exhibited it is not possible to give a strict definition which will classify a dense fluid as either liquid or gas.

Since two phases are essential for the recognition of the liquid state it is only when represented by a statepoint inside the dotted curve (Fig. 30) that a system can be said to be partly in the liquid state. Since the dotted curve of Fig. 30 extends only up to a certain temperature, there is some temperature for each gas above which the gas cannot be liquified. This temperature is called the *critical temperature*. It is given by the highest point of the dotted curve, where the left and the right branch come together or where the three roots of (484) coincide. It is accordingly the critical point defined on page 229.

It is possible by passing through a temperature above the critical point to change a system from the liquid to the gaseous state, or vice versa, without permitting a separation into two phases. For example, a container completely full of liquid CO_2 at 20° C. may be heated at constant volume to some temperature above the critical temperature and then expanded to a large volume. Upon cooling at 20° the CO_2 is in the same state, i.e. gaseous, as it

would have been following an isothermal evaporation, but the transition has been effected without discontinuity, since, by avoiding the area under the dotted curve (Fig. 30) the system has been kept out of the two phase region. The path of this change is shown by the line *LMNO*, Fig. 30.

The critical phenomenon explains the failure of the early attempts to liquefy the so-called " permanent " gases. Since the critical temperatures of O_2, N_2, H_2, etc. lie far below ordinary temperatures, it was impossible to produce liquefaction until investigators realized the necessity of cooling the gas. The whole subject was clarified by the classical experiments of Andrews [1] on the equation of state of carbon dioxide. Some of his original data are plotted in Fig. 31. It is seen that the curves have the same general shape as those of van der Waals' equation (Fig. 30).

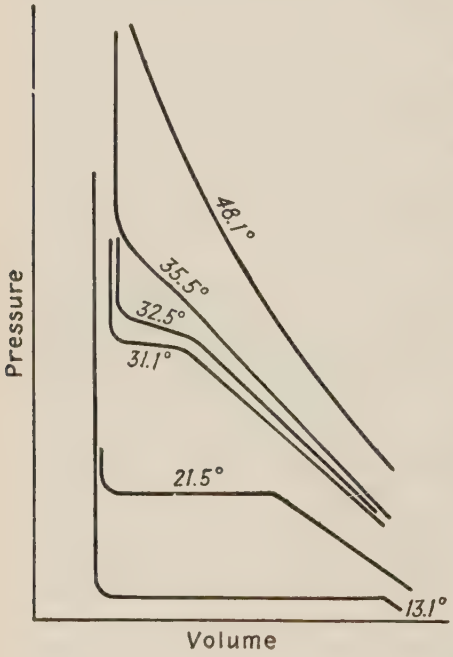

Fig. 31

The critical temperature may be interpreted as that temperature below which the effect of the attractive forces exerted by the molecules on each other is greater on the average than the effect of their thermal motion, provided they are brought sufficiently close together. The critical temperature is therefore an important quantity in that it is related to the intermolecular forces in a manner similar to that of the Sutherland constant C (p. 128), the latent heat of evaporation, etc.

Experimentally the critical constants (p_c, V_c and T_c) are extremely difficult to determine with accuracy. The maximum of the dotted curve of Fig. (30) is so flat that it cannot be found accurately by extrapolation. The empirical rule of Cailletet and Mathias [2] known as the " Law of the Rectilinear Diameter," has been used for the extrapolation of experimental data. This law states that the mid points of the lines *ABC* of Fig. 30 fall upon a straight line. The rule, however, is not obeyed accurately.

The critical data have been used for the determination of the van der Waals' constants a and b. From equations (485) and (486) it follows that at the critical point

[1] Andrews, *Phil. Trans.*, **159**, 575 (1869); **161**, 421 (1876).

[2] Cailletet and Mathias, *J. Physique*, [2] **5**, 549 (1886); *Compt. rend.*, **109**, 1563 (1897).

$$-\frac{RT}{(V-b)^2}+\frac{2a}{V^3}=0, \tag{488}$$

and

$$\frac{2RT}{(V-b)^3}-\frac{6a}{V^4}=0, \tag{489}$$

Solving these for a and b it is found that

$$b=\frac{1}{3}V_c, \tag{490}$$

$$a=\frac{9}{8}RT_cV_c. \tag{491}$$

Substitution in the equation

$$\left(p_c+\frac{a}{V_c^2}\right)(V_c-b)=RT_c \tag{492}$$

gives another expression for b, namely

$$b=\frac{1}{8}\frac{RT_c}{p_c}. \tag{493}$$

According to this treatment therefore

$$p_cV_c=\frac{3}{8}RT_c \tag{494}$$

compared with

$$pV=RT \tag{455}$$

for an ideal gas.

Since the critical point is far outside the region of validity of van der Waals' equation it is not surprising that the values of b calculated from (490) do not agree with those obtained from (493). a and b are determined accurately from the pressure-volume relationships of the gas in the region to which van der Waals' equation applies. As a matter of fact V_c is found to be more nearly equal to $2b$ than $3b$ as predicted by equation (490).

Similarly RT_c/p_cV_c is found to equal approximately 3.5 rather than 2.67. A few experimental values of these quantities are tabulated below:

TABLE VII

Gas	$\frac{V_c}{b}$	$\frac{RT_c}{p_cV_c}$
Oxygen	1.46	3.419
Nitrogen	1.50	3.421
Argon	1.41	3.424
Hydrogen	2.80	
CO_2	1.86	3.61

The pressure volume relationships of gases are frequently expressed by plotting isothermal values of pV against p as in Fig. 32. A gas in the perfect state gives of course the horizontal line I. At temperatures far above the critical the pV product rises steadily (Curve II). Under this condition the gas is less compressible than is to be expected from Boyle's Law. At lower temperatures the pV product goes through a minimum (Curves III and IV) which becomes more and more sharp as the temperature decreases. The vertical portion of curve IV corresponds to the liquid-vapor transition.

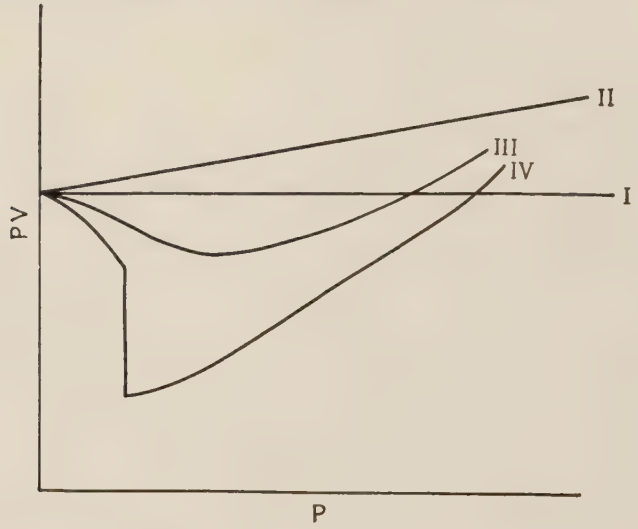

FIG. 32.

These curves may be interpreted by rewriting van der Waals' equation in the form

$$pV = RT + bp - \frac{a}{V} + \frac{ab}{V^2}. \tag{495}$$

If a is small in comparison to bpV and pV^3, the last two terms of this equation are negligible and pv increases linearly with p. Curve II therefore represents a gas at such a temperature that the effect of the intermolecular forces is negligible in comparison to the effect of the size of the molecules. Hydrogen and helium are exceptional in that they exhibit this property even at room temperatures.

If both a and b must be taken into account, the a/V term predominates at low pressures and the pV product decreases. As the pressure increases all of the last three terms on the right increase but since the last term increases more rapidly than the other two ($\sim 1/V^2$), the curves rise in all cases at sufficiently high pressures.

At the minimum of curves of the type of curve III $\partial(pV)/\partial p = 0$. The gas therefore obeys Boyle's Law at this point. That temperature at which the pV-p curve approaches the ordinate $p = 0$ with a horizontal tangent is known as the Boyle point. At this temperature the gas starts off in conformity with Boyle's Law and the corresponding curve marks the boundary between curves of type II and those of type III.

Another interesting development is the so-called " reduced equation of state " in which the pressure, volume and temperature of the gas are expressed as fractions of the corresponding critical constants. The resulting variables are spoken of as " reduced " magnitudes and are defined by the equations

$$\pi = \frac{p}{p_c}, \tag{496}$$

$$v = \frac{V}{V_c}, \tag{497}$$

$$\tau = \frac{T}{T_c}. \tag{498}$$

If these quantities are substituted in van der Waals' equations together with the values of a and b given by equations (490), (491) and (493) the result is

$$\left(\pi + \frac{3}{v}\right)(3v - 1) = 8\tau. \tag{499}$$

This equation is independent of the nature of the gas but unfortunately it is not able to express the experimental data with accuracy. It is possible to suppose, however, that there should be a general equation in which the only constants which occur would be universal numbers, applicable to all gases, provided the variables are measured in appropriate units, i.e., the reduced magnitudes. This equation need not be the particular law of van der Waals.

The law of corresponding states specifies then that there should be a universal equation of state of the type

$$\pi = f(v, \tau). \tag{500}$$

This may also be expressed by the statement that if any two gases have the same values of any two of the reduced magnitudes, they also have the same value of the third reduced magnitude. Kammerlingh-Onnes [1] has investigated the conditions that must be fulfilled by the molecules of two gases in order that they obey the law of corresponding states. He finds that the necessary conditions are that both the shape of and the forces exerted by the smaller molecules must become identical with those of the larger molecules if the dimensions and the forces of the smaller molecules are magnified by constant factors.

K. Wohl [2] has recently investigated the validity of the generalized theorem

[1] H. Kammerlingh-Onnes, *Amst. Akad.*, **21**, 22 (1888); *Arch. Neerl.*, **30**, 101 (1897).

[2] K. Wohl, *Zeit. f. Phys. Chem.*, **133**, 305 (1927).

of corresponding states for "normal substances" and finds it valid for the gaseous state up to the critical density (and pressure) with an accuracy of 1 per cent.

The General Equation of State: Throughout the discussion of the foregoing section it has been emphasized that van der Waals' equation gives only a qualitative description of the behavior of condensed gases and liquids. A very large number of attempts have been made to develop equations with wider range of applicability. Such equations have been for the most part semi-empirical in that their deduction has rested on unwarranted assumptions and further that they contain several arbitrary constants. Their usefulness consists in that they afford a condensed summary of experimental data. Among the more important equations of state are: van Laar's [1] equation, which retains the general form of van der Waals', but assumes that both a and b are functions of the volume and the temperature,

$$\left(p + \frac{a_g}{V(V+c)}\right)\left(V + \frac{b_g}{1 + \dfrac{b_g - b_0}{V}}\right) = RT, \tag{501}$$

where

$$a_g = a_\infty e^{\alpha/RT}; \qquad b_g = b_\infty e^{\alpha/RT}, \tag{502}$$

Clausius'

$$\left(p + \frac{a}{T(V+c)^2}\right)(V - b) = RT, \tag{503}$$

Berthelot's [2]

$$\left(p + \frac{a}{TV^2}\right)(V - b) = RT, \tag{504}$$

Dieterici's [3]

$$p(V - b) = RTe^{-\frac{a}{RTV}} \tag{505}$$

and Wohl's [4]

$$p = \frac{RT}{V - b} - \frac{a}{V(V - b)} + \frac{c}{V^3}. \tag{506}$$

$$a = \frac{a'}{T}, \qquad c = \frac{c'}{T^{4/3}}.$$

K. Wohl [5] has compared it with measurements on normal substances and finds good agreement for densities below the critical but acknowledges that it is not suited for higher densities.

[1] J. J. van Laar, Die Zustandsgleichung von Gasen und Flussigkeiten, Leipzig, 1924.

[2] D. Berthelot, J. Physique, III, **8**, 263 (1899).

[3] C. Dieterici, *Wied. Ann.*, **66**, 826 (1898); **69**, 685 (1899); *Drud. Ann.*, **5**, 51 (1901).

[4] A. Wohl, *Z. physik Chem.*, **87**, 1 (1914); **99**, 207, 226, 234 (1921). See also R. Wegscheider, *Z. physik. Chem.*, **99**, 361 (1921).

[5] K. Wohl, *Zeit. Phys. Chem.*, **133**, 305 (1927), **135**, 368 (1928), see also R. Wegscheider, *Z. Phys. Chem.*, **135**, 362 (1928) who points out the errors for $V < V_c$.

Keyes [1] has found the equation

$$p = \frac{RT}{V - Be^{-\frac{\alpha}{V}}} - \frac{a}{(V - l)^2}$$

to represent the behavior of Ar and N_2 well.

Beattie [2] has proposed the equation

$$p = \frac{RT(1 - \epsilon)}{V^2}(V - B) - \frac{A}{V^2}$$

$$A = A_0\left(1 - \frac{a}{v}\right); \qquad B = B_0\left(1 - \frac{b}{v}\right); \qquad \epsilon = \frac{c}{VT^3}$$

and has proved that it gives very accurate results for He, Ne, Ar, H_2, N_2, O_2, CO_2, CH_4 and ethyl ether in the general range of $-252°$ C. to 400° C. and up to 100 or 200 atm. It even represents the behaviour of a mixture of N_2 and CH_4 without new constants, but it must be pointed out that it contains five adjustable constants.

A very complete list of equations of state is given by J. Otto.[3]

The most useful equation is that of Kammerlingh Onnes,[4] which contains no assumptions. It is a formal development

$$pV = A + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^4} + \frac{E}{V^6} + \frac{F}{V^8}, \tag{507}$$

where A, B, C . . . are termed the first, second, third, etc. virial coefficients. These quantities are functions of the temperature and are expressed

$$B = b_1 + \frac{b_2}{T} + \frac{b_3}{T^2} + \frac{b_4}{T^4} + \ldots, \tag{508}$$

$$C = c_1 + \frac{c_2}{T} + \frac{c_3}{T^2} + \frac{c_4}{T^4} + \ldots. \tag{509}$$

Since the gas must be ideal at large volumes

$$A = RT. \tag{510}$$

For a moderately dense gas the equation may be written

$$pV = RT\left(1 + \frac{B}{RTV} + \ldots\right). \tag{511}$$

[1] F. G. Keyes, *Proc. Nat. Acad.*, **3**, 323 (1927).

[2] J. A. Beattie and O. C. Bridgeman, *Journ. Am. Chem. Soc.*, **49**, 1665 (1927), **50**, 3133, 3152 (1928), *Am. Acad. of Arts and Sc.*, **63**, 229 (1928); J. A. Beattie, *Jour. Am. Chem. Soc.*, **51**, 19 (1929), J. A. Beattie and C. K. Lawrence, *ibid.*, **52**, 6 (1930).

[3] *Handb. der Experimentalphysik*, Vol. 8, 2nd half, p. 224, Leipzig, 1929.

[4] Kammerlingh-Onnes, Comm. Phys. Lab. Leiden, No. 118*b*, (1910).

In the case of van der Waals' equation this becomes

$$pV = RT\left[1 + \frac{1}{V}\left(b - \frac{a}{RT}\right) + \ldots\right]. \tag{512}$$

In general, equations (508) and (512) have the form of equation (475).

$$B = N\left\{\int \epsilon dV + \frac{1}{2kT}\int \epsilon^2 dV + \frac{1}{6(kT)^2}\int \epsilon^3 dV + \ldots\right\}. \tag{513}$$

From the way in which the second virial coefficient varies with temperature it is therefore possible to determine the subsequent integrals in (512) and draw conclusions concerning the law of interaction between the molecules. This has been done by Keesom [1] and Zwicky (cf. p. 241).[2] The most general treatment will include in ϵ repulsions as well as attractions and give accordingly not only a but also b.

Kessom has investigated the third virial coefficient in a similar manner.

The main results of the Kinetic Theory can be obtained from a very rough picture of the molecule, namely, the assumption that molecules are hard elastic spheres. These results could therefore be obtained from any molecular model. Hence the experimental determination of the type of interaction between molecules, i.e., the law of intermolecular force, must resort to second order effects which can be expected to vary with the law of force. The experimental data which have been used for this calculation are first, the variation of the van der Waals' constants a and b with the temperature and, second, the change of the viscosity with the temperature.

In both cases it is customary to assume that the force between two molecules may be regarded as the superposition of an attraction and a repulsion, the potential of the two being represented by

$$\frac{g_1}{r^n} - \frac{g_2}{r^m}, \tag{514}$$

where g_1 and g_2, n and m are constants for any particular molecule. This type of interaction does not depend upon the orientation of the molecules and must therefore be regarded as an average over all orientations unless the molecules are spherically symmetrical as in the case of the inert gases. The principal justification for this assumption is that it is the most general which has as yet yielded to mathematical treatment. Since the attraction exceeds the repulsion at large distances n must be greater than m. The problem is now to determine the four constants of equation (514).

The procedure developed by Lennard-Jones [3] is to calculate the variation of the " second virial coefficient "

$$B = RTb - a \tag{515}$$

[1] W. H. Keesom, *Physik. Z.*, **22**, 129, 643 (1921).
[2] F. Zwicky, *Physik. Z.*, **22**, 449 (1921).
[3] J. E. Lennard-Jones, *Proc. Roy. Soc.*, **106A**, 463 (1924).

with the temperature for various values of n and m in the same manner as does Keesom. Upon comparison with the experimental data it is possible in some cases to select a pair of values of n and m which give the best fit between the theory and experiment. Thus Lennard-Jones finds that the data for helium are best represented, if $n = 14\frac{1}{3}$ and $m = 5$. With these values of the exponents g_1 and g_2 are found to be 2.35×10^{-116} and 2.33×10^{-14} respectively. For gases other than helium and hydrogen the variation of a and b with the temperature does not change sufficiently with the law of force to permit a unique determination of n and m.

Keyes [1] has evaluated the equation of state for a gas which has an attraction due to quadrupoles while the repulsion goes with the inverse 15th power of the distance.

The recent development of the new quantum theory (see later) has made it probable that the repulsion is proportional to e^{-br} rather than to r^{-n}.

Chapman and Enskog (loc. cit.) have calculated the viscosity of a gas whose molecules repel according to the inverse n'th power formula. Lennard-Jones (loc. cit.) has extended these calculations to molecules exercising an arbitrary repulsion and an inverse third power attraction. From this he shows that the best agreement between theory and experiment is obtained for helium if $n = 14.6$, in good accord with the value deduced from the equation of state.[2]

The Nature of the van der Waals Forces: Recent developments have led to the belief that all forces are to be traced back to electrical phenomena. This trend is exemplified by the explanations of the van der Waals forces.[3] Disregarding ions such as are present in electrically dissociated gases, the molecule regarded as a whole is electrically neutral. There are different types of forces, which neutral particles can exert upon each other. One important group can be explained in the following manner. In spite of their electroneutrality, molecules can exert forces on each other just as two magnetic needles can exert forces on each other even though each is magnetically neutral, i.e. contains just as much positive as negative magnetism. The cause of this latter interaction is the fact that the two magnetic poles are not situated at the same point in the needle so that if one needle is brought up to another, in general one of the two poles will be more closely approached than the other. The situation in the case of molecules which are electrically neutral as a whole is entirely similar. The molecules are neutral because they contain just as many positive charges in the nuclei (Rutherford-Bohr atom) as negative charges (electrons) in the outer parts of the atoms. They exert forces on each other

[1] F. G. Keyes, *Chemical Rev.*, **6**, 175 (1929).

[2] For a review of this work see "Interatomic Forces" by J. E. Lennard-Jones, Chap. X of R. H. Fowler's "Statistical Mechanics," Cambridge University Press, 1929.

[3] It can be shown that both gravitational and magnetic forces are much too small to have any influence on the equation of state. Thus, the work done by gravitation on the approach of two hydrogen atoms to a distance of 10^{-8} cm. is of the order of 1.7×10^{-44} ergs, kT at 1° Abs. is 1.3×10^{-16} erg. The work of attraction of two "Bohr magnetons," that is, of magnetic forces such as occur in atoms, is 7×10^{-18} ergs. See for a general review F. G. Keyes, *Chem. Rev.*, **6**, 175, 1929, and K. F. Herzfeld, *Handb. d. Phys.*, XXII, Leipzig, 1926.

because the positive charges are not situated at exactly the same points as are the negative charges. The law of force depends essentially upon the symmetry of the distribution of the charges. The simplest case is that of a " dipole " in which one positive charge is separated by a small distance from a negative charge. This system has the symmetry of a magnetic needle in that it has a negative and a positive pole. The fields have the same character in each case and the distributions of the lines of forces are of the same type. Examples of such dipoles are: sodium chloride vapor, which consists of positive sodium ions and negative chlorine ions, all acids,[1] water vapor, and so forth.

The force due to a single charge varies inversely with the square of the distance, according to the Coulomb law, but the force between dipoles decreases with the *third* power of the distance and is also a function of the relative orientation. The next symmetrical arrangement is the " quadrupole," of which there are two types: First, two dipoles may be laid end to end so that similar charges coincide. In this case there is obtained a rod on which the arrangement of charge is: positive charge—double negative charge—positive charge or vice versa. The second type is formed by laying two dipoles with their opposite charges next to each other forming a rectangle with charges of alternating sign at the corners. In both cases the opposite charges screen to the outside, that is, neutralize each other, still better than in the dipole. The field surrounding a quadrupole decreases with the fourth power of the distance. The usual diatomic gases, H_2, O_2, etc., are of this symmetry. It is possible to build up systematically still more symmetrical configurations in which the charges screen each other to a larger extent and for which, therefore, the field decreases still more rapidly with the distance. For a given type of structure the force naturally increases with the amount of the charges and with their distance apart, e.g., the effect of a dipole is measured by its moment which is $\mu = ed$.

But there exists an inherent difficulty of explaining attractive forces in this way. An investigation of the action between two magnetic needles shows that if the pole of one points toward the center of the other, there is no action; that there is an attraction if the positive pole of one points toward the negative pole of the other or vice versa; and that there is a repulsion if poles of the same sign point toward each other. If, now, such dipoles rotate as a result of their thermal motion, they will assume first a position in which they attract, then one in which they repel, and so on, if they are indeed independent of each other. The same is true of configurations other than dipoles, the so-called multipoles. In fact it may be shown that, in a uniform independent rotation, the attraction and repulsion just compensate each other. The electrostatic reason for this is that the number of lines of force emanating from a body is defined by the total charge on that body. Therefore, on the whole, no lines of force can proceed from a molecule which is neutral as a whole, so that all the lines of force leaving the molecule must return to it. The only effect of the *type* of distribution and symmetry of the charges within the molecule is to alter the distribution of the lines of force leaving and returning through the surface.

[1] See also K. Fajans, *Die Naturwissenschaften*, **11**, 165 (1923).

This does not change the argument since all the lines of force going out through any point of the surface must come back through some other point of the surface. The last statement means, however, that, on the average, the attraction and repulsion must compensate each other.[1] The attractive force which is actually present has been explained in two different ways:

(*a*) The first method was originated by Reinganum [2] and later extended by Keesom (loc. cit.). An independent uniform rotation of the molecules has been assumed, but it is pointed out that two molecules which interact spend a longer time, in proportion to the exponential $e^{\epsilon_r/kT}$, in those positions in which the potential energy is negative, i.e., where there is an attraction, than in those positions where the energy is positive and there is consequently a repulsion.

One point must here be emphasized which is entirely analogous to the previous discussion of the application of the barometric formula to a limited region of attractive forces (p. 117). There it was pointed out that a molecule *passing through* the particular region requires less time for the passage than would be required to traverse an equal interval in which there would be no attractive forces, because these forces increase the velocity of the molecule. The increased density of the molecules in regions of low potential energy depends on the fact that some cannot leave the region on account of their low velocity. The present situation is entirely similar. Suppose, for example, that a number of magnetized needles are placed in a magnetic field in such a way that they can rotate about axes perpendicular to the direction of the field. The needles can then execute two different types of motion. Those which have especially high velocities perform complete rotations. Their angular velocity is greatest when they are in a position of attraction and they therefore spend less time in this region. Those, however, which have not enough energy to execute complete rotations, oscillate about the direction of attraction until they experience a collision with another needle. It is the presence of these which causes more particles (molecules or needles) to have, on the average, the direction of the attractive force rather than the opposite direction.[3]

Keesom, in calculating the average attraction, extends the integral of state over the different orientations and uses as energy the potential energy of two molecules as a function of their mutual orientation. This function depends upon the structure of the molecule (dipole, quadrupole). He calculates the characteristic constants of the molecule which enter the equation (radius and electrical magnitudes) from the measured dependency of a upon the temperature. The data for H_2 and O_2 are well represented by assuming the corresponding molecules to be quadrupoles.

As has been stated, the van der Waals forces must vanish at high temperatures according to this treatment. As a matter of fact, Keesom's series begins

[1] The mathematical expression of this is that the product of two different spherical harmonics vanishes upon integration over the entire sphere. The potential of any arrangement of charges can be expressed as a series of spherical harmonics.

[2] M. Reinganum, *Ann. Physik*, **10**, 334 (1903); **38**, 649 (1912).

[3] W. Pauli, *Z. Physik*, **6**, 319 (1921).

with a term proportional to $1/T$. This depends upon the fact, that in the integral the mean value of ϵ_p is 0, and agrees with the equation of state of Berthelot [1] which is valid for moderately compressed gases, where a is set proportional to $1/T$.

(*b*) Debye [2] has pointed out that contrary to this prediction the van der Waals forces do not vanish completely at high temperatures and, further, that there are gases, namely all monatomic gases, to which Keesom's explanation cannot apply for reasons deduced from the quantum theory. It will only be remarked here that it was not necessary to take into account the orientation of the atoms and further, that a specific heat of rotation is missing. In Debye's discussion the independent, constant rotation of the molecule is retained, but it is assumed that the *field* surrounding each molecule is no longer independent of the presence of the other molecules in the immediate neighborhood. In order to explain the meaning of this, consider a magnetized needle rotating, with constant velocity, not in the presence of another needle, but in front of a soft iron sphere. Then, as the magnetic north pole approaches the sphere, a magnetic south pole is *induced* in the latter which moves along the sphere corresponding to the motion of the north pole of the needle. If now, instead of the north pole, the south pole of the needle is brought up to the sphere, a north pole is induced in the sphere on the side toward the inducing pole, so that there is again attraction. The case is exactly similar if the magnetic needles are replaced with electric dipoles, quadrupoles, etc., and the iron sphere with a dielectric. The attractive action is therefore quite independent of the velocity of rotation and accordingly of the temperature, for if the velocity is increased, the period is correspondingly decreased. Thus, although each oscillation requires less time, there are now more oscillations in unit time so that the amount of action per second is independent of the velocity, provided that the temperature is sufficiently high to preclude association or the influencing of the rotation itself by the forces (the Keesom orientation effect).

Now aside from the dipole or quadrupole fields of the charges supposed in the molecule, the molecules may be regarded as dielectric spheres, for when placed in an electric field the positive parts of the molecule are shifted in the direction of the field and the negative parts in the opposite direction. If the field strength is not too great, the shift is small in comparison to the molecular dimensions and is proportional to the field strength, as is the case for a dielectric. Debye uses the molecular refraction as a measure of the polarisability or deformability in an electric field. The refraction gives the polarisability in the electric field of a light wave and is readily measured. He then calculates the mutual potential energy of two molecules at a definite distance and a definite mutual orientation due to the induction which the quadrupole [3] of one exerts upon the other and vice versa. He sets this quantity equal to $\overline{U}_p$, equation

[1] D. Berthelot, Sur les Thermometres a Gaz. Paris, 1903; W. Nernst, Theor. Chemie, 10th ed., p. 254, (Stuttgart 1921).

[2] P. Debye, *Physik Z.*, **21**, 178 (1920).

[3] H. Falkenhagen, *Physik. Z.*, **23**, 87 (1922) has carried out the calculation for the dipole gases.

(475). The van der Waals' constant a is then expressed in terms of the molecular magnitudes, i.e. first, the smallest radius r to which the integral is to be extended (the largest radius r_0 can be taken as infinite as a result of the rapid decrease of the force); secondly, the polarisability and the quantities determining the quadrupole field also enter a. Debye gives the connection between the van der Waals' a and the Sutherland constant C in the formula for the mean free path (p. 128 and equation 165).

Upon summarizing the action of two molecules, the following points must be considered.

The rigid quadrupole field of molecule I acts upon the rigid quadrupole field of molecule II and vice versa. Result: the Keesom forces of orientation which vanish at high temperatures and are very great at low temperatures:

The rigid quadrupole field of molecule I acts on the charge induced by it in molecule II and vice versa. This effect is independent of the temperature, but is weak; at high temperatures *it alone is effective*; the action of the induced charge I on the induced charge II is neglected.

It is permissible to assume that at ordinary temperatures and for the case of polyatomic molecules the Keesom effect of orientation predominates.

A quite different aspect of the question arises from the new quantum theory. According to it all " closed shells " act electrostatically as if they had spherical symmetry.[1] This means that all atoms whose outermost shells are full (rare gases; also the vapors of the second group of the periodic table have closed shells in this sense) have no electric field which could give the effects described above.

It is then necessary to attack the problem in a different manner. It is still too early to give a general theory, but an outline of the cases treated may be given as follows: Schrödinger has calculated a continuous distribution of negative electricity in a hydrogen atom, the main amount of which is concentrated in what we usually call the radius of the atom, but which in fact extends with sharply decreasing density to infinity. He was originally of the opinion that the electron is actually not a body, small compared with the radius of an atom, but distributed over a rather wide range as described above. At present, however, the general opinion favors more the old idea of a small electron and considers the electrical distribution calculated by Schrödinger as an average over the orbit of the electron which will therefore usually be not farther than 10^{-8} cm. from the nucleus but which will, with decreasing frequency, reach out quite far from time to time.

Upon the close approach of two atoms the orbits will influence each other. Different types of influence must be treated separately.

In the case of two hydrogen atoms, two different things can happen.[2] If the electrons in the two atoms happen to have their spins (intrinsic magnetic

[1] A. Unsöld, *Ann. Physik*, **82**, 355 (1927).

[2] W. Heitler and F. London, *Z. Physik*, **44**, 455, (1927); Y. Sugiura, *Z. Physik*, **45**, 484 (1927); F. London, Quanten theorie u. Chemie, p. 59, Leipzig, 1928.

fields) parallel to each other, there will be repulsion only, increasing strongly with decreasing distance (van der Waals *b*). If on the other hand the two spins happen to be opposite, there is attraction at great distance, up to an equilibrium position, after which there is increasing repulsion. The latter behavior explains the formation of the H_2 molecule.

It is difficult to explain the nature of this attraction in the terms of macroscopic physics. Perhaps it may be interpreted as follows: In the new quantum theory, there is always the possibility of a process called the "exchange of electrons between the atoms." This probability increases with decreasing distance. It might then be considered that a pair of shared electrons (Lewis-Langmuir) are present for an increasing fraction of the time, this pair binding the two atoms.

The attraction described above is distinctly of a chemical nature. In the case of two H atoms (van der Waals *a*) the calculations have been made by Wang [1] who estimated their (second order) mutual perturbation and found a resulting potential energy of attraction

$$-\frac{243}{28}e^2\frac{r_0^5}{r^6}$$

where r_0 is the radius of the first Bohr orbit. This can be interpreted classically as the attraction induced in one atom by the rotating dipole formed by nucleus and electron of the other atom in the way considered above under *b*)

Slater [2] and Pauling [3] have performed similar calculations for He.

As far as repulsion goes, one type has appeared above in the case of the two H atoms. This has been extended by Slater and Pauling to He. Furthermore, Unsöld [4] has shown that a nucleus is repelled if it gets close enough to a negative ion, as it penetrates the "cloud" of negative electricity and is then closer to the positive nucleus, compared with part of the negative cloud.

Slater and Kirkwood [5] have generalized the results for attraction and repulsion to all non-dipole gases and have computed the equation of state with the method described on p. 238 for He and H_2. They find good agreement with experiment.

Eisenschitz and London [6] gave a similar deduction. They showed especially that Wang's results follow in general from a consistent use of the "method of perturbation."

The Ideal Liquid: It was pointed out in the discussion of the imperfect gas that the problem becomes extremely complicated if the mean free path is no longer large in comparison with the molecular dimensions. In the study of the liquid state these difficulties become still greater.

[1] L. C. Wang, *Phys. Zeit.*, **28**, 663, 868 (1927).
[2] J. C. Slater, *Phys. Rev.*, **32**, 349 (1928).
[3] L. Pauling, *Chem. Rev.*, **5**, 173 (1928).
[4] A. Unsöld, *Z. Physik.*, **43**, 563 (1929).
[5] We are indebted to Dr. Slater for permitting the use of this unpublished material.
[6] R. Eisenschitz and F. London, *Z. f. Phys.*, **60**, 491 (1930).

Here again three quantities [1] must be distinguished: (1) The kinetic pressure, p_t, due to the momentum transported in unit time through unit area of an imaginary surface.[2] This momentum is again subdivided into the following two parts: [3] (*a*) that carried by molecules whose centers pass through the surface, which has the magnitude RTc, and (*b*) that carried by molecules whose centers do not pass through the surface but which are reversed by collisions with other molecules before more than a segment of the molecule has penetrated the surface (jumping of momentum). This last portion increases rapidly with decreasing volume and cannot, in general, be calculated. (2) The second quantity is the internal or cohesion pressure which is caused by the mutual attraction of the molecules and acts as if the surface layer [4] surrounding the liquid were an elastic skin. (3) The third quantity is the external pressure which compensates that part of the thermal pressure not accounted for by the cohesion pressure.

In order to extend the calculations, Jäger [5] has introduced the conception of the "ideal liquid" as a mathematical simplification. The molecules of such a perfect liquid are to be as close together as are the molecules of a real liquid, but they are still to behave as if they were perfectly rigid, elastic spheres and, furthermore, the attractive forces are to change so slightly with the distance that clusters are formed only to a negligible extent. In other words, the ideal liquid is not associated.

Vapor Pressure: Jäger has given a kinetic deduction of the following formula for the vapor pressure p_s of an ideal liquid

$$p_s = p_t e^{-\frac{L_v}{RT}}.^{6} \tag{516}$$

The number of molecules condensing in unit time on unit area of the surface of the liquid is, as usual, equal to

$$c_s N_A \sqrt{\frac{kT}{2\pi m}} = p_s N_A \sqrt{\frac{1}{2\pi MRT}}. \tag{517}$$

If the molecules must do work to the amount $-\epsilon_p = L_v/N_A$ to escape from the liquid through the surface layer (which is considered infinitely thin), the

[1] R. Clausius, *Pogg. Ann.*, **157**, 168 (1850); J. D. van der Waals, Kontinuität des gasförmigen and flüssigen Zustandes. Leiden 1873, translation into German, Leipzig, 1881, 2d ed., 1899, see p. 53 et seq.

[2] If the transport in only one direction is considered, the momentum must be multiplied by two to take account of reflection at the wall. This is not necessary if the momentum coming from both sides is considered.

[3] G. Jäger, *Wien. Ber.*, **105**, 15 (1896).

[4] G. Bakker has devoted numerous articles to an investigation of the capillary layer from the standpoint of van der Waals' theory. He summarized his results in *Z. physik. Chem.*, **102**, 10 (1923).

[5] G. Jäger, *Ann. Physik.*, **11**, 1077 (1903).

[6] G. Jäger, *Wien. Ber.*, **99**, 681, 860 (1890); W. Voigt, *Gott. Nachr.*, 341 (1896); 19, 261 (1897); C. Dieterici, *Wied. Ann.*, **66**, 826 (1898).

number escaping in unit time per unit area would be

$$c_l N_A \sqrt{\frac{kT}{2\pi m}} e^{-\frac{L_v}{RT}} = p_l N_A \sqrt{\frac{1}{2\pi MRT}} e^{-\frac{L_v}{RT}} \tag{518}$$

if the liquid had the properties of a perfect gas, since in that case the number of collisions from the inside with unit area of the surface in unit time would be given by $c_l N_A \sqrt{kT/2\pi m}$ where c_l is the number of molecules per cubic centimeter of the liquid. The corresponding thermal pressure of the liquid then would be $p_l = c_l RT$. Because the molecules take up a large part of the space (volume correction) the number of collisions with the surface, and, by the same factor, the thermal pressures are increased.[1] Conversely it can be said that the number of molecules actually espacing is to the number that would escape from a perfect gas as p_t is to p_l.

The number of evaporating molecules is therefore

$$p_t \times N_A \sqrt{\frac{1}{2\pi MRT}} e^{-\frac{L_v}{RT}} \tag{519}$$

and, upon equating the number evaporating to the number condensing, equation (516) is obtained for the equilibrium pressure p_s. It has been assumed throughout this deduction that b is constant.

The Viscosity of Perfect Liquids:[2] The explanation of the viscosity of liquids can be obtained from the mechanism previously employed in the discussion of the viscosity of gases, namely a consideration of the transport of the X-component of momentum along the Z-direction through a substance placed between two horizontal planes. The upper plane is, as before, supposed to be moving in its own plane along the X-axis. Each molecule moving downward through a horizontal section 1 sq. cm. in area and at a height z_0, transports the X-component of momentum

$$m\left(W_x + \frac{\partial W_x}{\partial z}\Lambda\right), \tag{520}$$

where Λ is the distance from the section under consideration to the place where the molecule last collided, that is, the place where it assumed the velocity with which it crosses the section. The X-component of this latter velocity is, on the average, W_x. For a gas Λ is large in comparison to the diameter of the molecules, but in the present case this is not true. The molecular concentration is now so great that when a molecule is accelerated in some direction by a collision it experiences another collision so soon that its center has not had a chance to move a large distance. The distance traversed by the momentum from one collision to another is not in general equal to the distance traveled

[1] The calculation assumes that no forces act on the molecules when they are below a definite limiting surface, accordingly the thermal pressure extends very nearly to this limiting surface.

[2] G. Jäger, *Wine. Ber.*, **111**, 697 (1902).

by the center of the molecule, but is equal to the distance between the points at which collision occurs. In the case of a gas, this distance is mainly given by the distance traveled by the center, but here, since the distance traversed by the center of the molecule is small in comparison to the diameter of the molecule, the distance between the points at which two successive collisions have occurred is approximately equal to the distance between the two points on the surface of the molecule at which it has undergone collision. Therefore, the mean distance traversed between two collisions is to be regarded as approximately equal to the chord drawn between the two points of contact. This chord may be shown to be equal to r, the radius of the molecule (cf. note 1, p. 220). Hence the excess of momentum transported by each molecule moving down over that transported by a molecule moving in the opposite direction, in other words, the downward flow of momentum per molecule is

$$m\left(W_x + \frac{\partial W_x}{\partial z} r\right) - m\left(W_x - \frac{\partial W_x}{\partial z} r\right) = 2rm \frac{\partial W_x}{\partial z}. \tag{521}$$

Upon comparing the thermal pressure of an ideal gas to that of a liquid, at the same temperature it is seen that the impulse due to collision of a single molecule with the surface is the same in each case, the larger thermal pressure of the liquid being due to the much greater number of collisions with the surface. The ratio of the number of molecules moving through a plane in a liquid to the same number in a gas can therefore be set equal to the ratio of the thermal pressure of the liquid to the pressure of the gas. The number of molecules moving downward in the liquid is then

$$\frac{N_A}{2} \frac{p_t}{M w_t} \tag{522}$$

and the viscosity coefficient is

$$\eta = \frac{N_A}{2} \frac{p_t}{M w_t} 2rm = \frac{p_t}{w_t} r. \tag{523}$$

If $p_t = 13000$ atm., $\eta = 0.01697$ and $t = 0°$ C., r is found to be 3×10^{-8} cm.

Absolute Dimensions of Molecules:[1] Numerical values of molecular magnitudes will be summarized in this section. The experimental data from which they have been calculated were taken from the tables of Landolt-Börnstein, 5th ed. Berlin (1923).

Table VIII lists a number of mean free paths calculated from equation (248), which at 0° C. and 1 atm. reads

$$\Lambda_{273} = 0.1867 \frac{\eta_{273}}{\sqrt{M}}. \tag{524}$$

The tabulated values of Λ_{273} are expressed in centimeters. According to the

[1] For a more extended treatment of this subject see K. F. Herzfeld, *Jahrb. Radioakt. und Elektronik*, **19**, 259 (1922); "Grosse und Bau der Molekule," Handbuch der Physik, Vol. XXII.

discussion on p. 127, however, the mean free path is diminished by the attractive forces between the molecules. The mean free path which would obtain if the paths were rectilinear is found from the relation

$$\Lambda_\infty = \Lambda_{273}\left(1 + \frac{C}{273.1}\right), \tag{525}$$

where C is the Sutherland constant. Λ_∞ would be the mean free path at infinite temperature and a molecular concentration equal to that at standard conditions ($V = 22{,}390$ cc.) provided that the molecules of the gas could be regarded as infinitely hard spheres. In the third column of Table VIII are tabulated the values of C, in the last column the values of Λ_∞.

TABLE VIII

Gas	$\eta_{273}.10^7$	C	$\Lambda_{273}.10^5$	$1+\frac{C}{273.1}$	$\Lambda_\infty 10^5$
H_2	849	83	1.116	1.304	1.456
N_2	1,678	118	0.592	1.432	0.848
O_2	1,920	138	0.634	1.505	0.954
HCl	1,379	——	0.426	——	——
CO	1,672	100	0.590	1.366	0.806
CO_2	1,380	239.7	0.389	1.877	0.730
He	1,879	70	1.753	1.256	2.201
Ne	2,981	56	1.238	1.205	1.492
Ar	2,102	142	0.622	1.520	0.945
Kr	2,334	188	0.478	1.688	0.807
X	2,107	252	0.345	1.923	0.664

The diameter of the molecules can be obtained from the relation

$$\left.\begin{aligned} d^2 &= \frac{1}{\sqrt{2}\pi N_A c}\cdot\frac{1}{\Lambda\left(1+\frac{C}{T}\right)} = 8.323\times 10^{-21}\frac{1}{\Lambda_\infty} \\ &= 4.561\times 10^{-20}\cdot\frac{\sqrt{M}}{\eta_{273}}\cdot\frac{1}{1+\frac{C}{273.1}}. \end{aligned}\right\} \tag{526}$$

In this calculation it is assumed that the molecule is spherical. Rankine [1] has made various assumptions in regard to the shape of polyatomic molecules For example, he assumes diatomic molecules to be ellipsoids of revolution of definite excentricity, and then applies equation (248) using instead of the cross section of a sphere, the *average* cross section of the ellipsoid. The figures given in the second column of Table IX are calculated for spherical molecules. The

[1] A. O. Rankine, *Proc. Roy. Soc.*, **98A**, 360, 369 (1921); **99A**, 331 (1921).

(diameters in this and the following table are expressed in Ångstrom units 10^{-8} cm.).

In the next two columns are given values of d calculated from the van der Waals b by means of the equation

$$d^3 = \frac{3b}{2\pi N_A}, \tag{527}$$

$$d = 0.9234 \sqrt[3]{b} \times 10^{-8} \text{ cm.} \tag{528}$$

As a result of the inexactitude of van der Waals' equation, however, b cannot be determined uniquely. Thus, it can be calculated either from

$$b = \frac{V_c}{3} = \frac{M}{3\rho_c} \tag{529}$$

or the equation

$$b = \frac{RT_c}{8p_c}. \tag{530}$$

Table IX contains the values of d calculated from each of these equations.

In the fifth column is listed the values of d calculated from the assumption that the molecules are spherical and, in the liquid, packed as closely as possible. The density used in these calculations is that corresponding to the lowest temperature for which the measurements have been carried out

$$d^3 = \frac{6M}{\pi\rho_l}\frac{0.74}{N_A}, \tag{531}$$

$$d = \sqrt[3]{\frac{M}{\rho_l}}\, 1.326 \times 10^{-8} \text{ cm.} \tag{532}$$

0.74 is the fraction of the space filled by spheres when packed as closely as possible. The temperature of the density measurement is included in the column. A similar consideration together with a formula for the viscosity in terms of the molecular diameter, enabled Loschmidt in 1861 to calculate for the first time the number of gas molecules in 1 cc.[1]

TABLE IX

Gas	d from η	d from b		d from V_l at t° C.	Nuclear distance d' from I
		b from p_cT_c	b from V_c		
H_2. . . .	2.39	2.81	2.50	3.94(−258)	0.48
N_2. . . .	3.13	3.18	2.86	4.23(−202)	1.10
O_2. . . .	2.96	3.00	2.45	3.88(−227)	0.85
HCl . .	—	3.25	2.85	4.18(−83)	1.28
CO . . .	3.22	3.22	2.86	4.25(−205)	1.14
CO_2. . .	3.39	3.29	2.92	4.60(−34)	1.95

[1] The numbers in the corresponding row of the previously cited article (*Jahr. Radioakt und Elektronik* **19**, 290, 291 (1922) are too large by the constant factor 1.585 = $\sqrt[3]{4}$.

The last column of the table lists the nuclear distances (d') derived from the optically determined moment of inertia of the molecule according to the formula

$$I = d'^2 \frac{m_1 m_2}{m_1 + m_2}$$

or

$$\log d' = \tfrac{1}{2} \log I + \tfrac{1}{2} \log \frac{M_1 + M_2}{M_1 M_2} + 11.89131. \qquad (533$$

Thus, if the three atoms of CO_2 are assumed to be in a straight line, the carbon atom being in the middle, d' is the distance between the nuclei of the oxygen atoms.[1]

TABLE X

Gas	d from η	d from b		d from V_l at t° C.	d from the lattice constant of the solid	Ionic Distance	
		b from p_c, T_c	b from V_c				
He . . .	1.88	2.71	2.52	4.00(−271.5)	—	Salt	
Ne . . .	2.36	2.43	—	—	—	NaF	2.322
Ar . . .	2.97	3.00	2.92	4.04(−189)	3.84	KCl	3.140
Kr . . .	3.23	3.22	—	4.48(−146)	—	RbBr	3.441
X. . . .	3.54	3.21	3.10	4.43(−102)	—	CsI	3.94

The corresponding data for the inert gases are given in Table X. The next to the last column of this table gives the distance between the mid points of two adjacent atoms in the crystal lattice of the solidified gas.[2] The last column lists the distances between the midpoints of adjacent ions in the crystal lattices of the corresponding salts. In each case the electronic structures of the two ions of the crystal are the same, according to Bohr, as that of the inert gas. Thus, for example, Na^+ and F^- have the same structure as neon. The positive ion, however, has a greater nuclear charge (11 in the case of sodium) and the negative a smaller nuclear charge (9 in the case of fluorine) than the corresponding inert gas (10 in the case of neon). On account of this the positive ion may be expected to be slightly smaller and the negative slightly larger than the inert gas atom.[3]

[1] See also the data given by R. Birge, *Int. Crit. Tables*, Vol. 5, p. 409, 1929.

[2] F. Simon and C. v. Simson, *Z. Physik*, **25**, 160 (1924).

[3] Cf. H. G. Grimm, *Z. physik. Chem.*, **98**, 390 (1921).

CHAPTER V

THE SOLID STATE OF AGGREGATION

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The ordinary conception of a solid represents it as a portion of matter possessing rigidity—that is, offering resistance to forces tending to deform it. Solids differ from fluids in not being subject to flow. Such a distinction has little value from the scientific standpoint because of its indefiniteness; for flow can be induced in nearly any solid by the proper application of a sufficiently great force. A much more fundamental distinction among the states of matter follows from the recognition of the fact that the majority of substances can exist in solid forms which are bounded by plane surfaces so oriented to one another that the whole possesses some degree of symmetry. A substance in this state is said to be crystalline and the state is called the crystalline state of aggregation. All other solid bodies are classed as amorphous and are to be regarded as nothing other than liquids of great viscosity. Among such substances are glasses and resins.

That amorphous solids differ from liquids only in degree is demonstrated by the fact that on heating they lose, by imperceptible gradations, their rigidity and may become as fluid as water. The absence of a definite transition point renders it futile to attempt to distinguish such bodies as solid under one set of conditions and liquid under another. With crystalline solids, however, matters are very different. Every crystalline solid has a definite transition point at which it undergoes an abrupt change into a liquid with absorption of heat. Amorphous solids can be regarded as partaking in that continuity of state which characterizes the transition from gas to liquid under given conditions. No such continuity characterizes the transition from crystalline to liquid state, so far as can be discovered. Investigations on the influence of tremendous pressures on the behaviors of crystalline substances have shown that the transition to the liquid state invariably takes place abruptly when a definite temperature, which depends upon the pressure, is reached.[1]

It may therefore be concluded that there is a fundamental difference between the crystalline and all other states of aggregation. From comparatively early times it has been believed that crystals are to be regarded as structures built up by the symmetrical arrangements of some ultimate units, as contrasted with the random arrangement of such units in fluids. The discovery by Friedrich and Knipping,[2] acting on a suggestion of Laue,[2] that crystals act

[1] See, e.g., Bridgman, *Proc. Am. Acad. Sci.*, **47**, 441 (1912).

[2] *Sitzber. K. Bay. Akad.*, June (1912). *Jahrbuch. d. Radioakt. u. Elektronik*, **11**, 308 (1914).

as three-dimensional optical gratings for X-rays, with all its results, has left little doubt that such is the case. The constituent atoms in a crystal are arranged in a definite pattern which is regularly repeated throughout the body of the crystal. In fluids, definite arrangements of atoms within the molecules undoubtedly persist, as witness the fact that liquids and vapors may be optically active, but the molecules themselves are distributed at random.[1]

The Elements of Crystallography

Crystal Form: A study of the forms which crystals assume has led to the recognition of certain general laws of crystal form and to a classification on the basis of the degree of symmetry possessed by such forms. This is embodied in the science of crystallography.

If different crystals of some pure substance which have been prepared by essentially similar processes are examined, they will be found to differ as to size and as to the extent of development of corresponding faces. These things depend, in a manner only incompletely known, upon the method of preparation. If, however, the angles formed by the intersection of corresponding faces on these different crystals are measured, it is found that these are always the same. This fact is embodied in the first law of crystallography—the law of the constancy of interfacial angles.

Even a cursory examination of a crystal is in many cases sufficient to convince one that the orientation of its faces is by no means random. Thus, the faces on crystals of sodium chloride obviously unite to form a cube. In the majority of cases, however, there are clearly present faces of different characters. These usually occur in groups of like faces arranged symmetrically with respect to the crystal as a whole. Such groups constitute a form.

The second law of crystallography deals with the orientation of the faces on a crystal with respect to one another. The crystal may be supposed to have running through it axes (known as axes of reference) with respect to which the faces may be placed in space. When these are suitably chosen, it is found that all faces cut a given axis at distances from the origin which stand to one another as small whole numbers, if they cut that axis at all—for they may alternatively be parallel to it. This is the second law of crystallography—the law of rationality of intercepts or indices.

It follows from the law of rationality of intercepts that there corresponds to each reference axis in a given crystal an indivisible unit of length in terms of which the intercepts of faces on that axis are expressible as small whole numbers. This unit may or may not be the same for the different axes of the crystal. The actual values of the unit for corresponding axes on individual crystals obviously depend upon the size of the crystals. The *ratios* of the units on the different axes are always the same for crystals of the same substances, however. This follows from the law of constancy of interfacial angles and is sometimes termed the law of constancy of axial ratios.

[1] See however liquid crystals and surface films.

For the axial ratios of a crystal, it is customary to choose the ratios of the intercepts of some characteristic face rather than the ratios of the above-mentioned units, some one intercept being taken as unity. The intercepts of all other faces can then be simply related to these. For example, in the mineral, barite, a face whose intercepts stand in the ratios 0.815 : 1 : 1.313 is chosen as the unit face. We may designate these as $a : b : c$. The symbols of all other faces can then be written in terms of these. Two such faces have intercepts which stand in the ratios 1.630 : 1 : 1.313 and 0.815 : ∞ : 0.328, respectively. These can evidently be written as $2a : b : c$ and $a : \infty b : \frac{1}{4}c$. The latter are known as the *Weiss symbols* of the faces. As these symbols are rather cumbersome, another set in which the smallest whole numbers expressing the *ratios of the reciprocals of the coefficients* of the Weiss symbols, is now universally used. These symbols are known as the *Miller indices* of the face. Thus, for the second of the two faces mentioned above, the Weiss symbols are $a : \infty b : \frac{1}{4}c$. The coefficients stand as $1 : \infty : \frac{1}{4}$. The reciprocals of these stand as 1 : 0 : 4. The Miller indices of the face are expressed as [104]. For the other face, the Miller indices are [122].

The Classification of Crystals: There are recognizable, on the majority of crystals, sets of faces similarly oriented with respect to the symmetry of the whole. Such a set is known as a *form.* Thus, the six faces of a cube together constitute a form, as do the eight faces of an octahedron. These forms can be gathered into groups which have the same axes, planes and centers—that is, the same elements—of symmetry. Such groups constitute the crystal classes, of which there are 32. Axes of reference may be chosen for each of these classes such that the indices of all the faces of any one form are the same. When this is done, it is found that the crystal classes can be grouped into sets for which the axes are the same as regards equality or inequality of their lengths and of the angles they make with one another. These sets are the crystal systems, of which there are seven. These seven crystal systems with their axes are:

I. *The Triclinic or Anorthic System:* Three axes of unequal length all inclined at unequal angles other than 90°, 60°, 45° or 30°.

II. *The Monoclinic or Monosymmetric System:* Three axes of unequal length, one at right angles to the other two, which are inclined to one another.

III. *The Rhombic or Orthorhombic System:* Three axes of unequal length but at right angles.

IV. *The Tetragonal System:* Three rectangular axes, two of which are of equal length.

V. *The Trigonal System:* Three axes of equal length, forming equal angles (other than 90°) with one another.

VI. *The Hexagonal System:* Three axes of equal length lying in the same plane and inclined at 60° to each other and a fourth axis perpendicular to them and unequal to them in length.

VII. *The Cubic System:* Three equal rectangular axes.

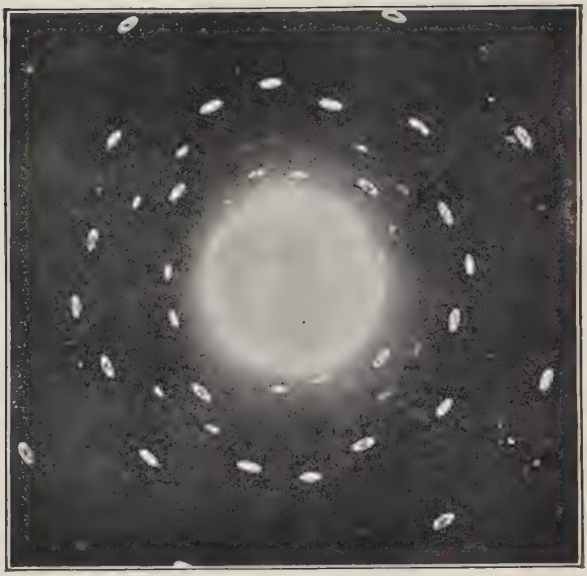
Crystal Structure

It was early recognized that the external form of crystals and their properties of cleavage indicated an internal structure consisting of some regular

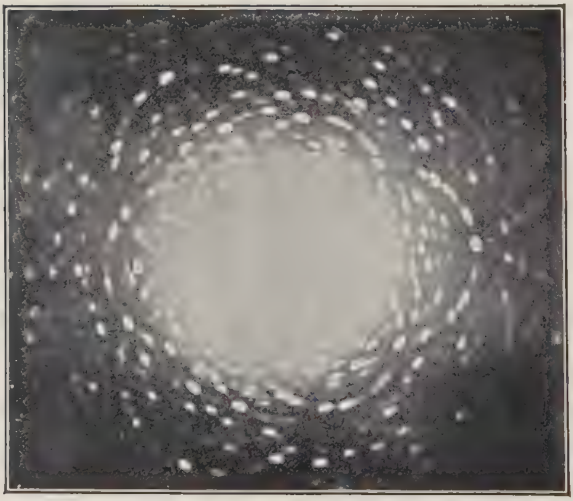
arrangements of ultimate units in space. Haüy, the discoverer of the law of rational indices, laid stress on the fact that when crystals of many substances, such as calcite and rock salt, are shattered, the fragments have the same form as the original crystals, and suggested that repetition of the process of fragmentation would eventually yield elementary particles (molecules integrantes) having the same form as the larger crystals. These elementary particles were regarded by Haüy as the "bricks" which form the complete crystal when packed side by side. He was able to show that this type of structure would account for the law of rational indices. Although this particular theory became somewhat discredited for many reasons, the fundamental idea has been retained. By degrees, however, the emphasis has been shifted from the elementary particle itself to its center of gravity or other point chosen the same for all the particles. These points can be thought of as arranged in some regular fashion on a three-dimensional trellis-work. Suppose that three sets of parallel planes interpenetrate, the distances between planes being the same in each set but in general different for the different sets. Then the lines in which the sets of planes, taken in pairs, intersect, represent the trellis-work, and the points at which the planes taken in threes (one from each of the three sets) meet, represent the positions at which the elementary particles may be placed. Such an arrangement is known as a space-lattice.

It is evident that as many interpenetrating space-lattices could be drawn as there are like points in the elementary particles. For example, one such lattice might be constructed for each atom in the molecule. Thus, if in calcite, the molecule $CaCO_3$ is taken as the elementary particle, five interpenetrating space-lattices of identical dimensions could be constructed, at the points of one of which would be placed the calcium atoms, of another the carbon atoms and of three others the three oxygen atoms. These five lattices may be regarded as derived from the fundamental lattice by translation. A new and more complicated arrangement of points in space obviously results. Such an arrangement of points is known as a *space-group*.

From considerations of symmetry, it has been found that only a restricted number of space-groups, obeying the law of rational indices, is possible. There are in fact just 230 such symmetrical arrangements of points in space. With respect to their symmetry, these 230 arrangements fall naturally into 32 classes which are identical with the 32 crystal classes. If the space-groups represent the actual grouping of atoms in crystals, it is obvious that there are many such groupings possible in the majority of the crystal classes, that is, there are a number of alternative arrangements of atoms which all have the same symmetry. The older method of studying crystals, based on the character of the faces developed, can usually establish the symmetry and therefore the class to which a crystal belongs, but gives no information as to the space-group, and therefore the actual arrangement of atoms. It is the great achievement of the X-ray method of analysis of crystal structure, which will now be discussed, that it was able to take this last step. By means of X-ray analysis, the arrangements of atoms in a large number of crystals have now been definitely established.



(*a*) Laue diagram of magnesium oxide



(*b*) Laue diagram of potash alum

TYPICAL LAUE DIAGRAMS

Diagrams by courtesy of Dr. R. W. G. Wyckoff.

X-rays and Crystal Structure: The investigations which have culminated in the determination of the arrangements of atoms in crystals with the help of X-rays had their beginning in attempts to obtain diffraction effects with X-rays. With an ordinary optical grating, there is no measurable diffraction, indicating that if X-rays are actually light waves, their wave-lengths must be very small even compared to that of visible light.[1] Various estimates had set these at 10^{-8} to 10^{-9} cm. Since the spacing of the lines of a grating must be of the same order as the wave-length of the light to be measured in order to obtain appreciable diffraction effects, it would obviously be impossible to prepare a grating which would diffract X-rays if their wave-lengths are as estimated, because the distance between lines would need to be comparable to the distances between the molecules of the solid.

It was suggested by Laue [2] (1912) that if crystals in reality represent orderly arrangements of atoms or molecules, they should act as three-dimensional optical gratings for X-rays, since various estimates had placed the distances between atoms in crystals at about 10^{-8} cm. The determination of the type of spectrum to be expected offered considerable difficulties, but Laue was able to show that if a beam of X-rays was thrown upon a crystal, it should be partially converted upon transmission through the crystal into a number of diffracted beams arranged symmetrically around the primary beam in a manner governed principally by the symmetry of the crystal. This should be revealed on a photographic plate, placed directly back of the crystal, by a central image surrounded by a symmetrical group of spots. Experiments, carried out by Friedrich and Knipping [3] soon after, completely confirmed the prediction. Two so-called Laue photographs of the diffraction patterns so obtained are shown in Plate 1.

This discovery not only demonstrated that X-rays were in reality light of short wave-length but also indicated that information as to the actual arrangements of the atoms or molecules in crystals could probably be obtained by this method. Because of the difficulty of the analysis and the almost complete lack of information as to the characteristics of either the X-rays or the atomic arrangements in the crystals, little use could be made of the results at the time. W. H. and W. L. Bragg [4] shortly afterwards devised a modification of the Laue method which first made possible direct determinations not only of the actual arrangements of atoms in many crystals but also provided a method of determining the absolute wave-lengths of X-rays.

The Bragg Method of X-ray Analysis: The space-lattice arrangement of atoms or molecules in a crystal indicates that the atoms or molecules can be regarded as occurring in parallel planes whose orientations are fixed by the law of rational indices and by the symmetry of the crystal. Each face of a crystal

[1] The wave-length of sodium — *D* line is 5896×10^{-8} cm.

[2] *Sitzber. K. Bay. Akad.*, June (1912). *Jahrbuch d. Radioakt. u. Elektronik*, **11**, 308 (1914).

[3] *Sitzber. K. Bay. Akad.*, June (1912).

[4] X-Rays and Crystal Structure, by W. H. and W. L. Bragg, 1915. See also W. H. Bragg, *J. Chem. Soc.*, **109**, 260 (1916).

is developed parallel to some one of these planes and the most frequently occurring faces are usually developed parallel to those planes which are richest in atoms or molecules, which are those planes of small indices. The Braggs were able to show that the diffraction of X-rays by a crystal could be just as satisfactorily and much more simply treated as reflections from these successive planes of atoms rather than as diffractions from a three-dimensional grating in which each atom represented a center of diffraction. In the Bragg method, X-rays composed principally of a single wave-length (i.e., " monochromatic " X-rays) are allowed to fall on a face of crystal. A reflection spectrum is obtained, that is, the monochromatic light is " reflected " at certain definite angles only. This is analogous to the reflection of visible monochromatic light by a stack of very thin plates of glass. The values of these angles vary with the angle of incidence of the beam, other things being equal. The problem is considerably simplified if only those cases are considered when the beam is " reflected " at an angle equal to the angle of incidence. Under these conditions, a very simple relationship exists between this angle, the distance between successive parallel planes and the wave-length of the X-rays.

In Fig. 2, p, $p \cdots$ are supposed to represent such planes parallel to some face of a crystal. Their common spacing is equal to d. $AA'A''A'''$ represents an advancing wave front of X-rays of wave-length $\lambda(AA_1)$. Consider those parts of this beam of X-rays which unite to give a reflection along BC. The distances traveled by different parts of the beam in going from $AA'A''A'''$ to C differ according as they are reflected from one or another plane. Thus, considering only the first two planes, the paths are ABC and $A'B'C$, respectively. The different parts of the beam, which are originally in phase, will not be in phase when they reach C, due to the difference in path, unless this difference is a whole number of wave-lengths. Except when this is the case, there will be no reflection at C, for the cumulative effect of even a slight difference in path between waves reflected by successive planes is sufficient to cause almost complete interference. The difference in path depends upon the value of the angle θ, other things being equal. Hence it is necessary to determine for what value of θ the difference in path is numerically equal to a whole number of wave-lengths.

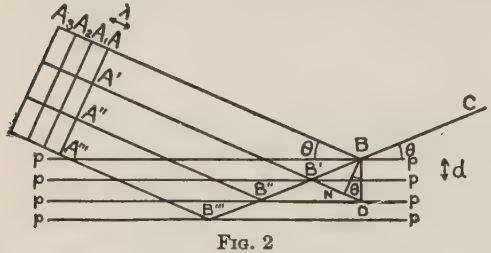


Fig. 2

Extend $A'B'$ to D and draw BD (which is perpendicular to the planes p, $p \cdots$). Draw BN perpendicular to $A'D$. The difference in length of the two paths ABC and $A'B'C$ is equal to

$$BB' - B'N = \Delta.$$

But

$$BB' = B'D.$$

Hence

$$B'D - B'N = ND = \Delta.$$

$$\frac{ND}{BD} = \sin \angle NBD.$$

But

$BD = 2d$, and $\angle NBD = \theta$, the angle of incidence.

Hence

$$ND = \Delta = 2d \cdot \sin \theta.$$

Maxima in reflection will occur when $\Delta (= ND)$ is equal to a whole number of wave-lengths, that is, to $n\lambda$, where n is a whole number. Hence, for this condition we have,

$$n\lambda = 2d \sin \theta.$$

The apparatus used by the Braggs (Fig. 3) is similar to a spectrometer (and is in fact used as such). In place of an ordinary grating, the crystal is mounted at the center of a turn-table having a graduated circle, with the face of the crystal normal to the table. X-rays from a suitable source are passed through absorbing screens to render them as nearly monochromatic as possible and then through two adjustable lead slits to obtain a well-defined beam. This beam is adjusted to strike the center of the crystal face, which is set on the axis of the turn-table in order that rotation of the turn-table will not throw it out of alignment. The reflected rays are received in an ionization chamber mounted on an adjustable arm whose posi-

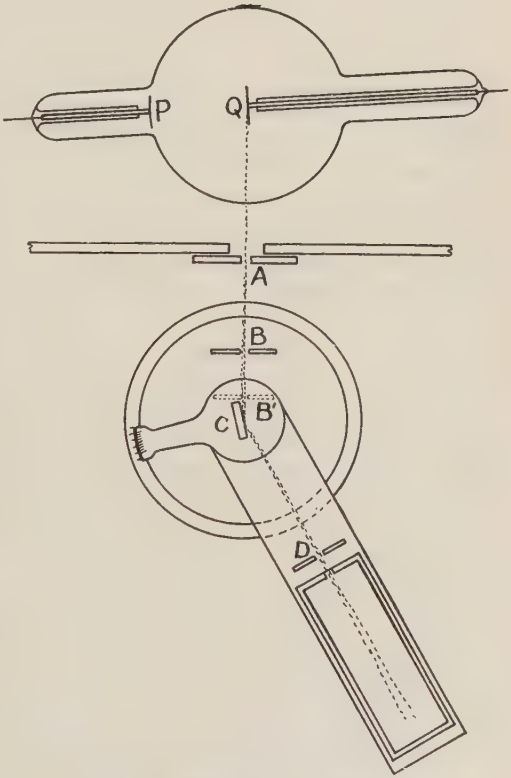


Fig. 3. Bragg's X-ray Spectrometer

tion relative to the crystal face can be read from a second graduated circle The ionization chamber contains some gas such as SO_2, which is easily ionized by X-rays, and is in connection with an electroscope, by means of which the intensity of the ionization and hence of the reflected X-rays can be determined. The crystal face and the ionization chamber are rotated about their common axis, keeping the angle between the face and the ionization chamber the same as that between the face and the incident beam,[1] and the strength of the ionization produced by the X-rays at different settings is measured. The settings corresponding to the maxima in reflecting power are thus determined. The corresponding angles between the face and the incident beam are those which should satisfy the relation,

$$n\lambda = 2d \sin \theta.$$

Since d and λ should be constant for any particular face and type of X-rays, it is evident that the values of sin θ should stand in the ratio of small whole numbers corresponding to the integral values of n.

$$\text{Sin } \theta = \frac{n\lambda}{2d} = nk$$

where k is a constant. This is found to be the case. Measurements on the cube face of NaCl gave maximum reflections at $\theta = 5.9°$, 11.85° and 18.15°, using X-rays from a palladium anticathode. The values of the sines of these angles are 0.103, 0.205 and 0.312, respectively, numbers which stand in the ratio of 1 : 2.00 : 3.03 or nearly 1 : 2 : 3, as was to be expected. From the above, the spacing of planes parallel to the cube face can be obtained in terms of λ, since the value of sin θ for a given value of n is known. Thus, in the above example, the value of d is

$$d = \frac{n\lambda}{2 \sin \theta} = \frac{1}{2(0.103)}\lambda = 4.85\lambda.$$

The analysis of crystal structure by the Bragg method consists in determining, by the means just outlined, the relative spacing of planes perpendicular to the principal directions through the crystal, by obtaining reflections of X-rays from the corresponding faces. These faces may be either those naturally occurring or ground on the crystal for this purpose. These relative spacings depend upon the arrangements of the structural units, that is, upon the fundamental space-lattices characteristic of each crystal system. If, therefore, the system to which the crystal belongs is known, the relative spacings to be expected for the different types of space-lattice possible can be calculated and compared with those found by X-ray analysis. Once the correct space-lattice has been determined, the absolute value of the spacing of the planes can be determined with the help of the density of the crystal and the Avogadro number (6.06×10^{23}). Knowing this, it is easy to calculate

[1] This involves rotating the chamber through twice the angle of rotation of the crystal face.

the value of λ; that is, the crystal can then be used as a reflection grating for the determination of the wave-length of X-rays.

The Crystal Structures of Sodium and Potassium Chlorides: The first crystals successfully studied by the Braggs were those of sodium and potassium chlorides. These both crystallize in the cubic system. There are three fundamental space-lattices possible to the cubic system. These are known as the simple cubic, the face-centered cubic and the body-centered cubic lattices. The whole space-lattice may be thought of as made up of a number of cells, among which the structural units of the crystal are distributed. Diagrams of such cells for the three cubic lattices are shown in Fig. 4. In the simple cubic lattice, one structural unit is associated with each corner of the cubic cell. In the face-centered cubic lattice, one unit is associated with each corner of

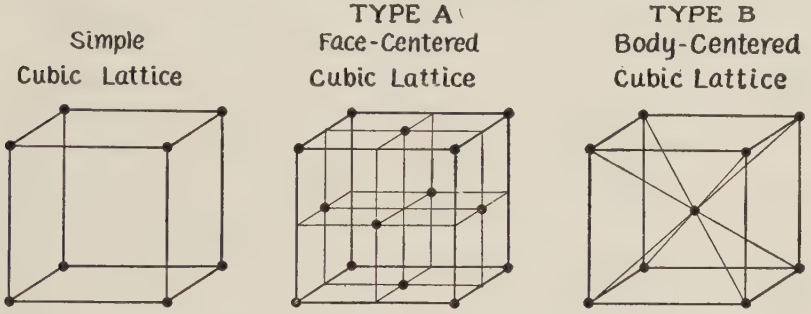


FIG. 4. Cubic Lattices

the cell and one with the center of each face. In the body-centered cubic lattice, one unit is associated with each corner of the cell and one with the center of the cell. We may calculate the relative spacing of the planes containing these units in planes parallel to the cube face, perpendicular to the face diagonal and perpendicular to the cube diagonal for the three types of lattice. Such planes are possible crystal faces and have the Miller indices (100), (110) and (111), respectively. The faces of the first type would be cube faces; of the second, faces of a dodecahedron; and of the third, faces of an octahedron. Their relative spacings for the three types of lattice are given below, that of the (100) planes being taken as unity.

	(100)	(110)	(111)
Simple cubic	1 :	$\frac{\sqrt{2}}{2}$:	$\frac{\sqrt{3}}{3}$
Face-centered cubic	1 :	$\frac{\sqrt{2}}{2}$:	$\frac{2\sqrt{3}}{3}$
Body-centered cubic	1 :	$\sqrt{2}$:	$\frac{\sqrt{3}}{3}$

The positions of the maximum reflections from the (100), (110) and (111) faces of crystals of sodium chloride with palladium X-rays [1] are shown in Fig. 5. The height of the lines indicates the intensity of the reflections. The first-order reflections occur at 5.9°, 8.4° and 5.2°, respectively, for the three faces. (The last, from the (111) face, is abnormally weak. The probable reason for this will be given later.) The sines of these angles are 0.103, 0.146 and 0.094, numbers which stand in the ratio of 1 : 1.42 : 0.91. Since

$$d = \frac{n\lambda}{2 \sin \theta},$$

the corresponding values of d should be in the ratios of the reciprocals of these numbers, which are 1 : 0.71 : 1.10. The ratios of d for the three faces in the face-centered arrangement are 1 : 0.71 : 1.15. The agreement indicates that the fundamental lattice is the face-centered.

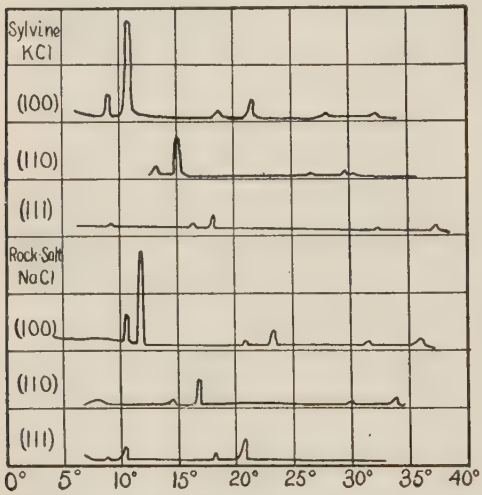


FIG. 5. Intensity of Reflections and Angle of Setting of Ionization Chamber

In the introduction to this section it was stated that we may associate with the points of the space-lattice the centers of gravity of the units of structure of the crystal or, if we wish, the atomic centers of any one kind of atom. Thus, if the structural unit in the sodium chloride crystal is the molecule NaCl, we may, if we wish, associate the centers of the chlorine atoms with the points of the fundamental lattice. Then, the centers of the sodium atoms will lie at the points of another lattice, identical with the fundamental one in dimensions but displaced from it in some direction, the two interpenetrating. Knowing that the fundamental lattice in a sodium chloride crystal is face-centered cubic, the problem of determining how the two lattices are oriented to one another is presented. It is known that the scattering power of atoms of a substance increases with the atomic weight. The X-ray reflections are due to scattering and since the chlorine atom is one and a half times as heavy as the sodium atom, it is probable that the reflections are mainly due to the chlorine atom lattice, though these will be altered somewhat by the presence of the sodium atom lattice. The only peculiarity noticeable in the sodium chloride X-ray spectrum is that the first order reflection from the (111) face appears to be abnormally weak and the third order spectrum is missing.

[1] The spectral line is in reality a doublet.

Suppose that the space-lattice carrying the sodium atoms is displaced from the fundamental space-lattice of chlorine atoms along the side of the fundamental cube half the length of the cube side. The effect of this will be to alternate sodium and chlorine atoms along each cube edge and give a "checkerboard" arrangement of atoms on the cube face. Such an arrangement, which is identical with the simple cubic arrangement except for the fact that it contains two kinds of atoms, is shown in Fig. 6, Type C. With this arrangement, the planes parallel to the cube faces contain both sodium and chlorine atoms in equal number and the spacing of these planes is the same as that of the fundamental face-centered lattice. The same is true of the planes parallel to the dodecahedral (110) faces. This arrangement will, however, bring planes containing only sodium atoms half-way between the (111) faces of the fundamental lattice. These planes must influence the reflections from the (111) faces. They would do so in the following manner. When the difference in path between waves reflected from two successive chlorine planes is equal to one wave-length, the difference of path between waves reflected from the sodium plane spaced half-way between and those reflected from either chlorine plane will be one-half a wave-length and therefore the two will be 180° out of phase. If the intensity of reflection from the sodium planes were exactly the same as that from the chlorine planes, there would therefore be no reflection whatever at the corresponding angle. If the reflection from the sodium plane is somewhat the weaker, the reflections from the chlorine planes will still be detectable but will be abnormally weak. This is what is found for the first order reflection from the (111) face of sodium chloride. The same will hold true for the third order reflection, when the waves from the sodium planes reach the ionization chamber $1\frac{1}{2}$ wave-lengths behind those from the chlorine planes. For the second order reflection the waves from the sodium planes are a full wave-length behind those from the chlorine planes and hence amplify the latter. The spectra are therefore what would be expected from this simple cubic type of lattice.

When a crystal of potassium chloride is examined, the spectrum (Fig. 5) is found to be of the same kind as that from sodium chloride except that the first order spectrum from the (111) face is completely lost. The arrangement of atoms is almost certainly the same as in sodium chloride but in this case the two kinds of atoms, potassium and chlorine, are of nearly the same mass and therefore reflect X-rays with so nearly the same intensity that the waves from the (111) potassium planes completely destroy those from the chlorine planes when the two sets are 180° out of phase.

The particular simple cubic or "sodium chloride" arrangement of atoms in sodium and potassium chlorides is therefore capable of accounting for the results. This, of course, does not eliminate the possibility of some other arrangement doing as well. This is very doubtful, however. An exhaustive investigation by Wyckoff [1] of such possibilities in the case of magnesium oxide,

[1] For an extensive bibliography and discussion of X-ray data concerning crystals see Wyckoff, *J. Franklin Inst.*, 195, 183, 349, 531 (1923), 'The Structure of Crystals,' Chem Catalog Co., New York.

which also apparently has the "sodium chloride" arrangement, indicates that no other simple arrangement will account for the results.

Granting that the simple cubic arrangement is correct, it is possible to calculate the distances between planes and hence to determine the wave-lengths

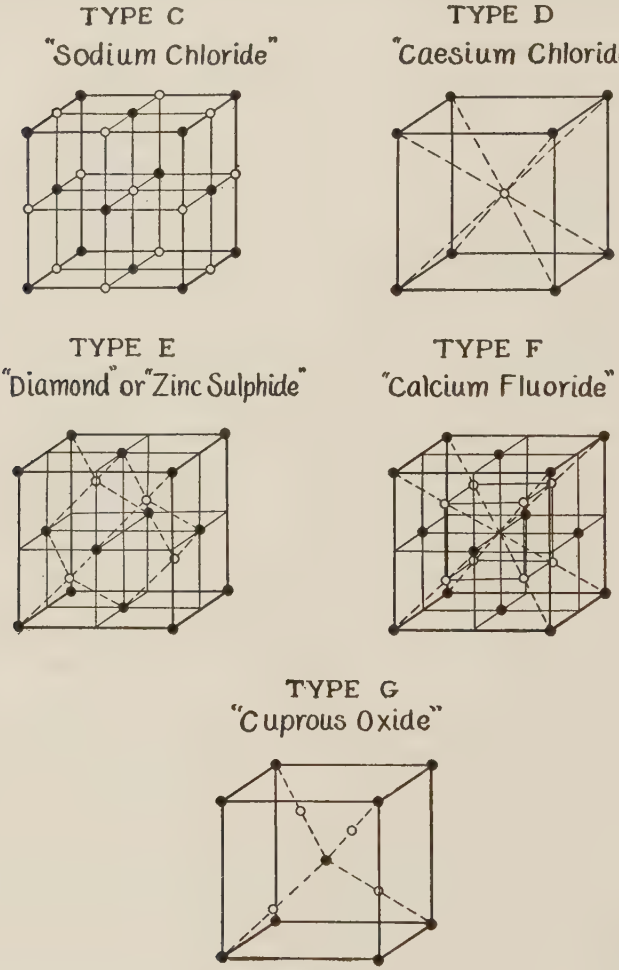


FIG. 6

of the X-rays used. We first wish to know the side-length of the elementary cubic cell. The first step is to determine the mass of substance, say sodium chloride, which is associated with each cell. The elementary cell has a chlorine atom at each cube corner and one at the center of each face. Since each atom at a cube corner is also associated with seven other cubes, only 1/8 of its mass

can be associated with the cube considered. But there are eight such atoms. Hence these altogether contribute the mass of one atom to the unit cell. Each atom in a cube face is associated with the adjacent cube and hence contributes only half its mass to the cube in question. The six such atoms altogether contribute the mass of three atoms to the cube. The total mass of chlorine to be associated with the unit cell is therefore equal to that of four chlorine atoms. Similarly it can be shown that four sodium atoms are to be associated with the cell. We may therefore say that the cell contains four molecules of sodium chloride. Now a gram molecule of sodium chloride occupies a volume of 27.0 cc. and contains 6.06×10^{23} molecules. The volume associated with four molecules is therefore

$$4 \times \frac{27.0}{6.06 \times 10^{23}} = 178 \times 10^{-24} \text{ cc.}$$

This is the volume of the unit cubic cell. The length of side of this cell is equal to the cube root of this number, which is 5.62×10^{-8} cm. Since one Ångstrom (Å.) is equal to 10^{-8} cm., this is 5.62 Å. The distances between planes parallel to a (100) face is equal to one-half of this value, or 2.81 Å. Having obtained a value for d_{100}, λ can be calculated. Using rays from a palladium anticathode, it was found that, for sodium chloride, $d_{100} = 4.85\lambda$, whence

$$\lambda = \frac{d_{100}}{4.85} = \frac{2.81}{4.85} = 0.58 \text{ Å.}$$

This is the wave-length of the characteristic X-rays from palladium. It is clear that by means of this method a crystal can be used to determine the wave-lengths of X-rays in a manner analogous to the determination of the wave-lengths of visible light with an optical grating. This is in fact the method by which the absolute wave-lengths of X-rays are calculated.

Modern Crystal Structure Analysis: The classical investigations of W. H. and W. L. Bragg have effectively opened up the field of crystal structure analysis by means of X-rays. Modern investigations of crystal structure, however, do not depend exclusively on this method. It has developed that the so-called Laue photographs when analysed with the aid of the crystallographic theory of space-groups [1] give much more precise information as to the details of the atomic arrangements. By this method it is possible to decide in the case of crystals of low symmetry especially what alternative arrangements are possible when a unique solution is not obtainable.

In addition to the above, a method has been developed for the examination of materials which cannot be readily obtained in the form of well-developed crystals. This so-called powder method is due to Debye and Scherrer,[2] and to Hull.[3] A beam of monochromatic X-rays is passed through a layer of the powdered material. A photographic plate placed behind the preparation

[1] See Wyckoff, The Structure of Crystals, Chem. Catalog Co., New York, 1924.
[2] *Physik. Z.*, **17**, 277 (1927); *ibid.*, **18**, 291 (1917).
[3] *Phys. Rev.*, **10**, 661 (1917).

records a system of concentric rings whose dimensions and relative spacings are dependent on the structure of the crystals.

The Powder Method as a Method of Chemical Analysis: In the powder method of X-ray analysis of crystal structure, a series of sharp lines, corresponding to the reflections from the various faces when the relation

$$n\lambda = 2d \sin \theta$$

is satisfied, are recorded on a strip of photographic film. These constitute a pattern which is unique for every substance. It has been shown by Hull [1] that this fact can be utilized in the qualitative analysis of substances in the solid state. For example, suppose that an ordinary chemical analysis in the wet way shows that a sample of crystalline solid in the form of small crystals contains Na, K, Cl and Br and it is desired to know what particular salts are present in the solid, whether NaCl and KBr or NaBr and KCl or all four. Ordinary analysis would be unable to show. If, however, the sample is ground to a powder and an X-ray photograph taken by the powder method, this will be immediately revealed, since each type of crystal lattice present will record on the photographic film its particular set of lines, which can then be identified by comparison with photographs obtained with the pure salts. From the relative intensities of the lines corresponding to the different substances, a rough quantitative estimate of the amount of each present can even be made.

Some Results of X-ray Analysis of Crystal Structure: The crystal structures of a relatively large number of substances crystallizing in the cubic system have been determined. Several types of arrangements of atoms are met with, drawings of which are shown in Figs. 4 and 6.

Type A is the face-centered cubic lattice (see Fig. 4). This is the structure of a large number of metals. It represents one type of arrangement which would result from the closest packing of spheres. An alternative arrangement resulting in a hexagonal structure is also met with and is described below. In both, each atom is equidistant from 12 others.

Type B is the body-centered cubic lattice (see Fig. 4). This is the structure of many of the metals. Each atom is equidistant from eight others.

Type C is known as the simple cubic or "sodium chloride" arrangement. This is the structure of the alkali halides (except the cæsium salts) and the alkaline earth oxides and sulphides. The two kinds of atoms are arranged on two face-centered lattices which interpenetrate in such a manner that they combine to give a simple cubic lattice.

Type D is known as the "cæsium chloride" arrangement. This is the structure of the cæsium halides, thallium chloride and the low temperature modifications of ammonium chloride and bromide. The two kinds of atoms are arranged on two simple cubic lattices which interpenetrate so as to bring the atoms of one kind at the centers of the cubes formed by the atoms of the other kind. The result is a body-centered lattice.

[1] *J. Am. Chem. Soc.*, **41**, 1168 (1919).

Type E is the "diamond" or "zinc sulphide" arrangement. It is based on a face-centered cubic lattice and represents the arrangement of atoms in the diamond and in silicon, germanium and grey tin. Many binary salts including zinc sulphide have the same type of lattice, the atoms of one kind occupying the positions at the corners and face centers of the cube and those of the other kind being at the centers of the alternate small cubes into which the face-centered arrangement can be divided. In crystals of diamond and of the other elements having this arrangement, the atoms of the element occupy *all* the positions. This arrangement is of particular interest in that it places each atom equidistant from four others. The closeness of the packing suggests that the atoms are held by primary valence bonds.

Type F is the "calcium fluoride" arrangement. It is one of the arrangements in which salts which contain two atoms of one kind and one of another crystallize. Examples are calcium, strontium and barium fluorides. In this arrangement, the atoms, of which kind there is only one in the molecule, let us say those of calcium in calcium fluoride, are arranged on a face-centered lattice. The atoms of the other kind, fluorine in this example, are arranged on two other face-centered lattices which penetrate the first so as to bring a fluorine atom at the center of each of the eight small cubes of the face-centered cube.

Type G is the "cuprous oxide" arrangement. This is the alternative cubic arrangement for compounds of the type AB_2 or A_2B and is the structure of cuprous and silver oxides. The simplest way of regarding the arrangement is to think of it as consisting of a body-centered lattice of the atoms of which there is only one in the molecule (oxygen, in the case of cuprous oxide, Cu_2O), penetrated by a face-centered lattice on which lie *all* the atoms of the other kind (copper in the case of cuprous oxide), bringing the latter atoms at the centers of the alternate small cubes into which the body-centered lattice is divisible.

Two other types of arrangements more or less frequently met with belong to the hexagonal system. These are the "hexagonal close-packed" and the "zinc oxide" arrangements.

The hexagonal close-packed arrangement is shown in Fig. 7. It represents the arrangement of atoms in many metals. The fundamental cell in this type is a prism with an equilateral triangle as its base. There is an atom at each of the six corners of this prism. Six of these prisms may be fitted together to give a hexagonal prism (shown in the figure). Three more atoms are now to be placed at the centers of alternate triangular prisms. These form part of a second lattice interpenetrating the first. When the ratio of the side to the altitude of the prism is as 1 : 1.633, the distance from one corner to the center of the prism is equal to the side-length. Under these circumstances each atom is equidistant from 12 others.

In the "zinc-oxide" arrangement two hexagonal close-packed arrangements, one carrying the zinc atoms and the other the oxygen atoms, interpenetrate. The resulting arrangement is difficult to visualize or to draw.

The essential point is that it brings the atoms of one kind into positions such that they are equidistant from four of the other kind. Consider one of those prisms of the hexagonal close-packed arrangements which contains an atom at its center. If the ratio of side to altitude is as 1 : 1.633, the atom at the center and the three atoms at the corners of the base are at the corners of a regular tetrahedron. In the "zinc oxide" arrangement an atom of the other kind will lie at the center of this tetrahedron. The "zinc oxide" arrangement, therefore, bears the same relation to the hexagonal close-packed arrangement as does the "diamond" to the face-centered cubic arrangement.

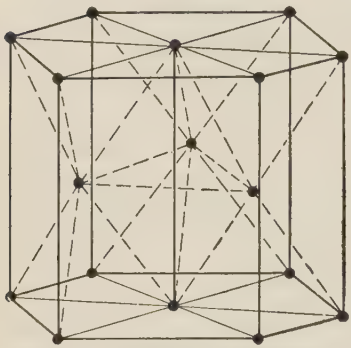


FIG. 7. Hexagonal Close-packed Lattice

One other type of structure is of special interest in connection with the subject of isomorphism. This is the "calcite" arrangement. The crystallographic axes are of equal lengths and inclined to one another at equal angles other than 90°. The unit cell may be regarded as a distorted cube. In calcite the calcium and carbon atoms are arranged in the same fashion as are the sodium and chlorine atoms in the "sodium chloride" arrangement, that is, the "calcite" arrangement might be characterized as distorted simple cubic. The oxygen atoms are arranged in sets of three around the carbon atoms and close to the latter, showing that the carbonate ion maintains its identity in the crystalline state. The minerals dolomite ($CaMg(CO_3)_2$), rhodocrosite ($MnCO_3$), and siderite ($FeCO_3$) and the compound $NaNO_3$ all have the calcite arrangement.

In the following table are given the type of arrangement, the length of side of the unit cell and the distance apart of nearest atomic centers in crystals of a number of substances. The types of arrangements are abbreviated as follows: face-centered cubic (F.C.C.), body-centered cubic (B.C.C.), simple cubic or "sodium chloride" (NaCl), "cæsium chloride" (CsCl), "diamond" (Diam.), "zinc sulphide" (ZnS), "calcium fluoride" (CaF_2), "cuprous oxide" (Cu_2O), hexagonal close-packed (H.C.P.), "zinc oxide" (ZnO). For the dimensions of the unit cell, the length of side is given for cubic crystals, and the side of the triangular prism and ratio of altitude to side for hexagonal crystals. The distance apart of atomic centers refers to the distance between nearest centers of like atoms in elements and of unlike atoms in compounds. Distances are given in Ångstrom units (1 Å. = 10^{-8} cm.).

The Structure of Crystals from the Chemical Standpoint. *Salts:* One of the most interesting facts which has developed from X-ray analysis of crystal structure is that in crystals of salts (including oxides and sulphides), the chemical molecule, as it is ordinarily thought of and as it would conceivably exist in the vapor phase, has completely lost its identity. Thus, in a crystal

TABLE I

CRYSTAL STRUCTURE AND INTERATOMIC DISTANCES

Elements				Compounds			
Substance	Type	Side of Unit Cell, Å.	Distance between Nearest Centers, Å.	Substance	Type	Side of Unit Cell, Å.	Distance between Nearest Centers, Å.
Al.....	F.C.C.	4.07	2.88	BeO.....	ZnO	2.70	1.65
Ca.....	"	5.56	3.93			(1.63)	
Ni.....	"	3.54	2.51	MgO....	NaCl	4.20	2.10
Co.....	"	3.55	2.51	CaO.....	"	4.76	2.38
Cu.....	"	3.61	2.55	SrO.....	"	5.10	2.55
Rh.....	"	3.82	2.70	BaO.....	"	5.48	2.74
Pd.....	"	3.95	2.80	NiO.....	"	4.15	2.08
Ag.....	"	4.06	2.87	CdO....	"	4.72	2.36
Ir.....	"	3.81	2.69	ZnO.....	ZnO	3.22	1.97
Pt.....	"	3.93	2.78			(1.60)	
Au.....	"	4.07	2.88	MgS....	NaCl	5.08	2.54
Ce.....	"	5.12	3.62	CaS.....	"	5.64	2.82
Pb.....	"	4.91	3.47	SrS.....	"	5.87	2.93
Th.....	"	5.10	3.56	BaS.....	"	6.40	3.20
Li.....	B.C.C.	3.50	3.03	MnS....	"	5.21	2.61
Na.....	"	4.30	3.72	PbS.....	"	5.80	2.90
K.....	"	5.20	4.50	ZnS.....	ZnS	5.42	2.35
V.....	"	3.04	2.63	CdS.....	ZnO	4.16	2.54
Cr.....	"	2.90	2.51			(1.62)	
Fe.....	"	2.86	2.47	SnS.....	"	3.60	
Mo.....	"	3.14	2.72			(2.20)	
W.....	"	3.15	2.73	SrSe	NaCl	6.20	3.10
Mg.....	H.C.P.	3.22	3.22	ZnSe....	ZnS	5.65	2.45
		(1.62)		LiCl	NaCl	5.17	2.59
Ti.....	"	2.97	2.97	LiBr....	"	5.48	2.74
		(1.59)		LiI.....	"	6.06	3.03
Co.....	"	2.51	2.51	NaF....	"	4.65	2.33
		(1.63)		NaCl....	"	5.63	2.91
Zn.....	"	2.67	—	NaBr....	"	5.95	2.98
		(1.86)		NaI.....	"	6.47	3.24
Zr.....	"	3.23	3.23	KF.....	"	5.36	2.68
		(1.59)		KCl.....	"	6.26	3.13
Ru.....	"	2.69	2.69	KBr.....	"	6.59	3.30
		(1.59)		KI.....	"	7.11	3.56
Cd.....	"	2.96	—	RbCl....	"	6.60	3.30
		(1.89)		RbBr....	"	6.93	3.47
Ce.....	"	3.65	3.65	RbI.....	"	7.36	3.68
		(1.62)		CsCl...	CsCl	4.12	3.56
Os.....	"	2.71	2.71	CsBr....	"	4.30	3.72
		(1.59)		CsI.....	"	4.55	3.94

TABLE I—*Continued*

Elements				Compounds			
Substance	Type	Side of Unit Cell, Å.	Distance between Nearest Centers, Å.	Substance	Type	Side of Unit Cell, Å.	Distance between Nearest Centers, Å.
C (diamond) . . .	Diam.	3.55	1.54	TlCl	CsCl	3.85	3.33
				AgCl	NaCl	5.54	2.77
Si	"	5.43	2.35	AgBr	"	5.77	2.88
Ge	"	5.62	2.44	AgI	ZnS	6.49	2.81
Sn (grey) .	"	6.46	2.80	AgI	ZnO	4.59 (1.633)	2.81
				CuCl	ZnS	5.49	2.38
				CuBr	"	5.82	2.52
				CuI	"	6.10	2.63
				CaF_2	CaF_2	5.49	2.38
				SrF_2	"	5.77	2.50
				BaF_2	"	6.20	2.69
				Cu_2Se . . .	"	5.75	2.49
				Cu_2O	Cu_2O	4.30	1.86
				Ag_2O	"	4.73	2.05

of potassium chloride, each potassium atom has equidistant from it six chlorine atoms, each of which in its turn is equidistant from six potassium atoms. No pair of potassium or chlorine atoms can be singled out and said to constitute a chemical molecule, since each atom belongs as much to five other atoms of the other kind as it does to the one with which it is arbitrarily paired.

Similar considerations apply to salts of oxygen acids so far as the disappearance of the molecule is concerned, but the association of the atoms of the acid radical apparently carries over into the crystal. Thus, in calcite, three oxygen atoms are grouped around each carbon atom, the distance between C and O centers being 1.28 Å. whereas the distance between the centers of the nearest Ca and O atoms is 2.42 Å.

Diamond and Graphite: With respect to the non-existence of any molecule in the ordinary sense, a crystal of diamond is similar to those of salts. Each carbon atom is surrounded by four others which are equidistant from it and each of these is in its turn surrounded by four. The structure may in fact be thought of as the ultimate in the branching of carbon chains, the crystal itself being a sort of giant molecule. The attachment of each carbon atom in diamond to four others of course recalls at once the quadrivalence of carbon in organic compounds. Another structural feature of carbon compounds which is discernible in the diamond lattice is the six-membered ring. This ring is made up of the atoms at the centers of three adjacent faces of the face-centered lattice and of three of the four atoms which lie at the centers of the small cubes.

The atoms are not all in one plane but the para atoms are one below and one above the plane of the other four. The rings are not isolated but are built out, as are those in naphthalene and anthracene, except that they are extended in two dimensions instead of one. Thus, each carbon atom occupies the ortho position in two rings and the para position in one. The rings occur in planes perpendicular to the body diagonal of the cubic lattice.

In graphite, the branched-chain structure of diamond is lost, but the ring structure remains. In diamond, the nearest atoms in two adjacent planes which contain the rings are 1.54 Å. apart, which is also the distance apart of adjacent atoms in the ring. In graphite, these planes have been separated till the nearest atoms in adjacent planes are 3.25 Å. apart (over twice as great a spacing as in diamond) and adjacent atoms in the ring have been drawn slightly together, their distance apart being 1.50 Å. The planes are not oriented to one another in quite the same way in the two structures. The relation between the two is shown in Fig. 8.

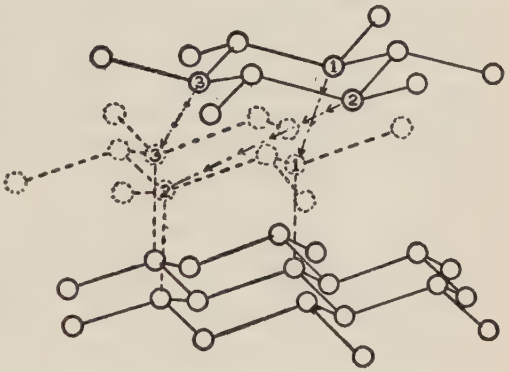


Fig. 8. Diamond-Graphite Relationship

The wide spacing of the planes in graphite leaves each atom closely attached to only three others. This fact, with the existence of the rings, suggests the planes in graphite as giant molecules of the aromatic series of the type of naphthalene and anthracene, the rings being extended in two dimensions. The weakness of the binding between adjacent planes is emphasized by the fact that the familiar cleavage of graphite occurs along these planes.

Organic Compounds: The X-ray analysis of crystals of organic compounds offers considerable difficulty because of their low symmetry and the unquestionable complexity of the arrangements. Some interesting beginnings have been made, however. Thus, Sir W. H. Bragg [1] has deduced probable structures for naphthalene, anthracene and some related substances. These are in agreement with the assumption that the six-membered ring as it exists in diamond and graphite is also present in these substances, as has been assumed in organic chemistry. The integrity of the molecule is thus in all probability maintained, contrary to the case in crystals of salts. Indeed, it is difficult to believe that it could have been otherwise when the almost infinite possibilities of rearrangement are taken into account. The fact that optically active substances are not racemized on crystallization, when so slight a change would accomplish this result if the arrangement were once broken up, is enough to establish this.

[1] *Proc. Phys. Soc. London*, 34, 33 (1921).

The structure of tartaric acid has also been recently investigated in Bragg's laboratory by Astbury.[1] Although the X-ray method is not capable of distinguishing between the enantiomorphous (mirror image) forms, the existence of a spiral arrangement was established.

Isomorphism: Many groups of substances which are similar in chemical constitution exhibit almost complete identity of crystalline form. Such substances are said to be isomorphous. Mitscherlich, who first observed the fact in connection with the rhombic forms of $Na_2HPO_4.12H_2O$ and $Na_2HAsO_4.12H_2O$, and who proposed the term isomorphism, believed that the identity of form was complete and assumed that the substances contain the same number of atoms arranged in the same fashion. Recent measurements by Tutton[2] on the rhombic sulphates and selenates and monoclinic double sulphates and selenates of the alkali metals have shown conclusively that the crystals of the members of these isomorphous series are not exactly alike but differ slightly in the values of the axial ratios, the variation in the latter and in various physical properties revealing a regular progression in passing from one member of the series to the next. This is illustrated by the following values of the axial ratios of the first series of substances. While the differences are slight, they are nevertheless real.

TABLE II

THE AXIAL RATIOS OF THE ISOMORPHOUS SERIES $R_2\begin{pmatrix}S\\Se\end{pmatrix}O_4$

(R = alkali metal. The crystals are orthorhombic)

Salt	Axial Ratios		
	a	b	c
K_2SO_4	0.5727	1	0.7418
Rb_2SO_4	0.5723	1	0.7485
Cs_2SO_4	0.5712	1	0.7531
K_2SeO_4	0.5731	1	0.7319
Rb_2SeO_4	0.5708	1	0.7386
Cs_2SeO_4	0.5700	1	0.7424

It is in general characteristic of isomorphous substances that when a solution containing two such substances is evaporated, the two will crystallize out together forming mix-crystals, which are single crystals containing both substances. Further, when a crystal of one such substance is placed in a super-saturated solution of another, the second substance will crystallize out or overgrow on the first just as it would on a crystal of itself. Molecules of such substances are therefore capable of fitting into or onto the crystal lattices of one another. These properties had acquired great importance as tests for isomorphism prior to the discovery of the X-ray method of analysis of crystal structure and had indeed been adopted by many writers as the essential prerequisites of isomorphous substances. This view has introduced many difficulties,

[1] *Proc. Roy. Soc.*, December, 1922.

[2] Tutton, Crystalline Structure and Chemical Constitution (MacMillan, 1910).

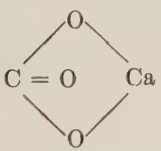
however, and has tended to complicate the whole subject. For example, sodium and potassium chlorides crystallize in the same forms and it is now known that they have the same crystal structures, yet they do not form mix-crystals. On the other hand, mix-crystals of potassium and ammonium chlorides, and of potassium and ammonium salts generally, may be obtained, although the crystals of these substances are not alike, though both are cubic, and the numbers of atoms in the molecule (though not the number of potential ions, of course) are different. It is probable that, in order that two substances shall form mix-crystals, it is necessary that the volume and general form of the structural units shall not be very different. Other agencies are undoubtedly at work, however, since mix-crystals of substances as different as ammonium chloride and ferric chloride can be obtained.

Another difficulty in the way of the use of mix-crystal formation as a criterion of isomorphism is that one of the substances considered may have a very low solubility. This difficulty is introduced in the case of sodium nitrate and calcium carbonate (in the form of calcite). These substances both crystallize in the trigonal system, forming rhombohedra whose axes are inclined to one another at almost the same angles, namely, 106° 33′ for sodium nitrate and 105° 5′ for calcium carbonate, and X-ray examination has shown that the two have exactly the same crystal structures (see above). The two substances are, therefore, isomorphous. In addition, their molecular volumes are not very different (in cc. per gm. mol., 37.5 for $NaNO_3$ and 36.9 for $CaCO_3$). Since, however, calcium carbonate is practically insoluble, mix-crystals cannot be obtained, though sodium nitrate can be made to overgrow on calcite.

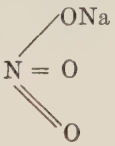
Because mix-crystals of sodium nitrate and calcium carbonate could not be obtained, even though this was for the practical reason that calcium carbonate is insoluble, it has been denied that the two are in fact isomorphous. The disinclination to regard them as isomorphous resulted from the fact that their structures were different on the old method of writing formulæ. Langmuir [1] has cleared up this and many other disputed cases of isomorphism by showing that on the basis of the Lewis theory of valence, the two have in fact the same structures, which are as given below.

Old Structures

Calcium Carbonate



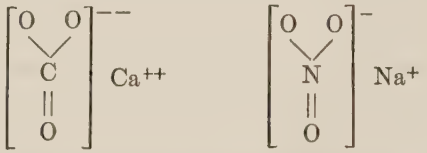
Sodium Nitrate



[1] Langmuir, *J. Am. Chem. Soc.*, 41, 1543 (1919).

New Structures

(A pair of shared electrons is represented by one bond.)



The only difference between the two is that in the first the ions are doubly charged and in the second they are singly charged.

Polymorphism: It often happens that a substance can occur in more than one crystalline form. When this is the case, the substance is said to be polymorphic. The different polymorphic modifications ordinarily belong to different crystal systems, though there are exceptions. A familiar example is sulphur, which has a rhombic modification, stable up to 95.6°, and a monoclinic modification, stable between 95.6° and 119.25° (its melting point).

Polymorphism results from different space-lattice arrangements of the same chemical units, as is attested by the fact that the modifications usually belong to different crystal systems. The crystal structures have only been worked out in a few cases. Thus, carbon occurs as diamond and as graphite, the structures of which have already been discussed. Silver iodide occurs in a hexagonal and in a cubic form. In the first, it has the ZnO structure and in the second, the ZnS structure. Ammonium chloride is an example of a substance having two modifications which both crystallize in the same system (the cubic). The high temperature modification has the sodium chloride structure and the low temperature modification has the cæsium chloride structure.

Polymorphic modifications may or may not be interconvertible. When they are interconvertible (e.g., $S_{rh} \overset{96.5°}{\rightleftharpoons} S_{monocl.}$), the change is said to be enantiotropic. When the change can only take place in one direction, that is, when one form is metastable under all conditions investigated, it is said to be monotropic, as Diamond → Graphite or Aragonite → Calcite. Since such forms as diamond and aragonite have remained as such through geologic ages, it is evident that the conversion of polymorphic modifications may be exceedingly slow. This is to be compared to the rapidity with which equilibrium is reached in the transition of solid to liquid. Further discussion of solid-solid transitions will be found in Chapter IX, "Heterogeneous Equilibrium."

Solid-Liquid Transition

The melting point of a pure crystalline solid may be defined as the temperature at which it is in equilibrium with the corresponding pure liquid. This temperature depends upon the pressure on the system, the variation being given by the Clapeyron equation.

It is probably safe to say that, as a general rule, a crystalline solid undergoes spontaneous transformation into the liquid phase when the melting point is reached; that is, a crystalline solid cannot be superheated. Nevertheless, it must be stated that, as experimentally determined, melting points sometimes appear not to be sharp. This was found to be the case for the silicate minerals, diopside, anorthite, and the like, by Day and Sosman,[1] and for betol and dextrose by Tammann.[2] These investigators found that, while melting always set in at a definite temperature, it was possible to heat the solid several degrees above this point during the process of melting. These results seem to show that melting takes place with independent finite velocity even above the melting point rather than that the rate is dependent solely upon the rate of supply of heat at the melting point.

The freezing point of a liquid is identical with the melting point of the corresponding solid when the latter is defined as the temperature at which pure solid and liquid are in equilibrium at a given pressure. The freezing point of a liquid does not mark off the limit of existence of the liquid phase, however, for if a liquid is carefully freed from suspended solid, especially particles of the corresponding solid phase, and is protected from vibrations and sudden changes, it may often be cooled many degrees below the freezing point. Under these conditions the velocity of crystallization may be negligibly small. It is to this possibility that glasses owe their existence. An extended study of the velocity of crystallization of supercooled liquids has been carried out by Tammann.[3] This investigator found that two factors have to be taken into account: (1) the rate of formation of crystal nuclei and (2) the rate of growth of the latter below the melting point. Both rates pass through maxima with diminishing temperature but the maxima occur at different points. With piperin, whose melting point is 129° C., the rate of formation of crystal nuclei was greatest at 40° C. and practically negligible above 80° and below 0° C. The rate of growth of the nuclei was a maximum at 100° and negligibly small at the melting point. Similar results were obtained for betol and a number of other substances. With many substances, however, the temperatures for the maximum rates of nucleus formation and nucleus growth lie so close to one another and to the melting point that measurements are difficult. For such substances practically no supercooling is possible.

Each polymorphic modification of a substance has its own particular melting point. For example, rhombic sulphur melts at 113° while monoclinic sulphur melts at 119.25°. Consequently, in giving a melting point, the polymorphic modification to which it refers should also be stated. Of two polymorphic modifications, that which is metastable in the melting point region has the lower melting point.

For further information on solid-liquid transitions, Chapter IX on Heterogeneous Equilibrium should be consulted.

[1] *Z. anorg. Chem.*, **72**, 1 (1921).

[2] *Z. physik. Chem.*, **68**, 252 (1910).

[3] See Tammann, Kristallisieren und Schmelzen, Leipzig, 1903; J. A. Barth. See also Chapter XV.

The Compressibility and Thermal Expansion of Crystalline Solids

The P, V, T relations of crystalline solids are complex and, as yet, the kinetic-molecular theory of the solid state is only in the preliminary stages of development. Part of this complexity arises from the fact that, except in the cubic system, the properties of crystals vary when measured in different directions through the crystal, that is, crystals are anisotropic. Thus, when a crystal of silver iodide is heated, it contracts in one direction while expanding in another.

It is generally assumed that the units of the crystal lattice (atoms or molecules) are confined as to motion to vibrations about equilibrium positions in the lattice. This equilibrium results from the action of attractive and repulsive forces between the constituents of the lattice. There has recently been much speculation as to the nature of these forces and of the characteristics of the motions of atoms in the lattice, references to which will be found in the sections on thermodynamics and quantum theory.

Numerous measurements of the P, V and V, T relations of solids have been made. These are usually stated in terms of the coefficients of compressibility and thermal expansion. The volume coefficients are

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \text{and} \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P.$$

These express the fractional change in volume per unit increase of pressure and of temperature. Sometimes the linear coefficients are given instead of the above. These refer to the fractional changes in length. For cubic crystals, whose properties are the same in three directions—and which are therefore isotropic—the linear coefficients are very nearly equal to 1/3 of the volume-coefficients.

The coefficients of expansion and compressibility are very small. Thus, the coefficients of compressibility for the solid elements vary from 61×10^{-6} for cæsium down to 0.16×10^{-6} for diamond. These are for pressures expressed in megabars [1] (10^6 dynes per sq. cm.). Values of the coefficients of compressibility and of expansion at 20° C. for a number of substances are given in Table III. There have also been added to the table the melting points, molecular volumes and crystal data.

It may be assumed that the atoms of a solid hold their normal distances apart as the result of a balance of attractive and repulsive forces. The attractive force gives rise to the cohesion of the solid. It is clear that thermal expansion must take place against this force and will therefore be small when the cohesive force is large. Compression, on the other hand, must take place against the repulsive forces. Since, however, the two are normally balanced against one another, the repulsive force must be large and therefore the compressibility small, when the cohesive force is large. These two properties should therefore vary from one solid to another in the same way and this is

[1] The megabar is 1.33 per cent less than the atmosphere.

TABLE III

PHYSICAL PROPERTIES OF SOLIDS

β = coefficient of compressibility $\times 10^6$, for pressure measured in megabars.
α = coefficient of thermal expansion, $\times 10^5$.
M.P. = melting point in degrees, absolute.
V = atomic or molecular volume in cc.
d = distance between nearest atoms in the crystal lattice, in Ångstroms ($= 10^{-8}$ cm.).

Substance	β	α	M.P.	V	Space-lattice	d
Li	9.0	19.0	453	13.1	B.C.C.	3.03
B	0.3	—	2800	4.7	—	—
C (diamond)	0.16	0.3	Very high	3.4	Diam.	1.54
C (graphite)	3.0	7.2	Very high	5.4	—	1.50
Na	15.6	22.0	371	23.7	B.C.C.	3.72
Mg	2.9	7.8	927	13.3	H.C.P.	3.22
Al	1.47	7.2	930	10.1	F.C.C.	2.88
Si	0.32	2.3	1733	11.4	Diam.	2.34
P (red)	0.52	—	863	14.6	—	—
P (white)	20.5	36.0	317	16.6	—	—
S	12.9	18.0	384	15.5	—	—
K	31.7	25.0	335	45.5	B.C.C.	4.50
Ca	5.7	—	1073	25.3	F.C.C.	3.93
Cr	0.9	—	1823	7.7	B.C.C.	2.51
Mn	0.84	—	1533	7.7	—	—
Fe	0.60	3.6	1790	7.1	B.C.C.	2.47
Ni	0.43	4.2	1725	6.7	F.C.C.	2.51
Cu	0.75	5.0	1356	7.1	F.C.C.	2.55
Zn	1.7	8.7(?)	692	9.5	H.C.P.	2.67
As	4.5	1.6	1073	13.3	—	—
Se	12.0	13.0	490	18.5	—	—
Rb	40.0	30(?)	312	56.0	—	—
Mo	0.46	1.1	2773	11.1	B.C.C.	2.72
Pd	0.54	3.8	1822	9.3	F.C.C.	2.80
Ag	1.01	5.7	1234	10.3	F.C.C.	2.87
Cd	2.1	7.4	594	13.0	H.C.P.	2.96
Sn	1.9	6.7	505	16.2	—	—
Sb	2.4	3.3	903	17.9	—	—
I	13.0	25.0	386	25.7	—	—
Cs	61.0	33(?)	301	71.0	—	—
Ta	0.53	2.3	3123	10.9	B.C.C.	2 83
W	0.27	1.1	3300	0.6	B.C.C.	2.73
Pt	0.38	2.7	2020	9.1	F.C.C.	2.78
Au	0.64	4.3	1336	10.2	F.C.C.	2.88
Tl	2.3	9.0	574	17.2	—	—
Pb	2.32	8.8	600	18.2	F.C.C.	3.47
Bi	3.0	4.0	543	21.2	—	—
NaCl	4.27	12.1	1077	27.1	NaCl	2.81
NaBr	5.24	—	1031	32.1	NaCl	2.98
NaI	7.05	—	926	40.8	NaCl	3.24
KCl	5.19	—	1045	37.6	NaCl	3.13
KBr	6.39	12.6	1003	43.4	NaCl	3.30

TABLE III—*Continued*

Substance	β	α	M.P.	V	Space-lattice	d
KI	8.75	12.9	953	53.1	NaCl	3.56
AgCl	2.38	13.2	724	25.8	NaCl	2.78
AgBr	2.75	10.5	700	29.0	NaCl	2.89
AgI	4.09	—	—	41.4	ZnS	2.81
TlCl	4.1	—	699	34.1	CsCl	3.34
TlBr	5.3	—	723	37.6	—	—
TlI	6.98	—	704	46.7	—	—
CaF_2	1.2	5.7	1575	24.7	CaF_2	2.35
MgO	0.70	2.8	3000	11.0	NaCl	2.10
PbS	1.95	6.0	1288	31.2	NaCl	—

found to be the case. Thus, among the solid elements, the alkali metals are found to have the greatest compressibilities and also the greatest expansion coefficients and correspond therefore to minima in the cohesive forces. Two other properties, atomic (or molecular) volume and melting points, in all probability also bear a relation to the cohesive forces. A large cohesive force should result in a relatively small atomic volume and a high melting point. The small atomic volume obviously corresponds to a large attraction between the atoms. The melting point represents the limit to which a solid can be heated and maintain its form. Rise in temperature corresponds to the input of energy, some of which, as kinetic energy, works against the cohesive forces. If these forces are small, a relatively small input of energy and therefore a relatively low temperature is sufficient to overcome them and bring about destruction of the lattice and hence melting.

Heat Capacities of Crystalline Solids

The Law of Dulong and Petit: The atomic heat capacities of a large number of crystalline solids when measured in the vicinity of room temperature approximate to the value 6 calories per degree. In so far as this applies to the elements, it is known as the law of Dulong and Petit. This is true of the metallic elements and of a number of halides and sulphides, as may be seen in the following table. The "atomic" heat capacities of compounds are calculated by dividing the product of specific heat and molecular weight by the number of atoms in the molecule. At the end of the table are given values for the atomic heat capacities of some of the lighter solid non-metallic elements and of solid compounds containing such elements as oxygen and carbon. It will be seen that these deviate markedly from the rule.

The above values are those determined at constant pressure. Lewis has shown that the values of the atomic heat capacity at constant volume, calculated from the above by the thermodynamic relation

$$C_v = C_p - 0.02423\frac{\alpha^2 VT}{\beta}$$

TABLE IV

ATOMIC HEAT CAPACITIES AT ROOM TEMPERATURE

Elements		Compounds	
	Atomic Heat Capacity		Atomic Heat Capacity
Li	6.6	NaCl	6.4
Na	6.9	KCl	6.2
Mg	6.0	KI	6.8
Al	5.8	AgCl	6.5
K	7.1	AgI	6.7
Ca	6.0	TeCl	6.3
Fe	6.0	PbS	5.9
Cu	5.8	$PbCl_2$	6.2
Zn	6.0	Sb_2S_3	5.7
Ag	6.1		
Pt	6.1	SiC	3.2
Te	6.4	MgO	4.8
Pb	6.3	CuO	5.2
		Al_2O_3	4.1
B	2.8	Fe_2O_3	5.1
C (diamond)	1.6	$CaCO_3$	4.1
C (graphite)	2.0	$H_2C_2O_4$	3.1
Si	4.5		
I	6.9		

in which

V = Atomic volume,
β = Compressibility,
α = Expansion coefficient,

are in somewhat closer agreement than the constant pressure values. There still remain marked deviations, however.

One reason for the partial failure of the law of Dulong and Petit lies in the arbitrary choice of room temperature as the temperature of comparison. Investigation of the change of heat capacity with temperature has revealed that this law is subordinated to a more general one which states that atomic heat capacity at constant volume increases with the temperature to a maximum value which is in the neighborhood of 6 calories per degree for all substances.[1] This constant maximum has already been reached at room temperature by those substances which obey the law of Dulong and Petit, and their heat capacities are nearly independent of the temperature at room temperature. The heat capacities of those other substances which deviate from the law are still increasing more or less rapidly with the temperature and presumably will reach a maximum at much higher temperatures. Thus, for example, the

[1]See, however, Eastman, Williams and Young, *J. Am. Chem. Soc.*, **46**, 1178, 1184 (1924).

atomic heat capacity of diamond has risen to 5.45 calories per degree at 1169° K., from the value of 1.6 calories per degree at room temperature.

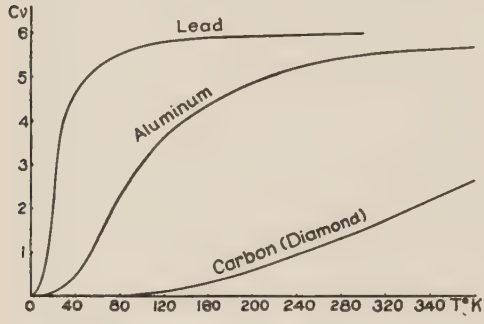


FIG. 9. Atomic Heats of Lead Aluminum and Diamond

Heat Capacity and Temperature: In Fig. 9 are plotted values of atomic heat capacity against temperature for three typical substances. It will be seen that for two of these the heat capacity approaches a value in the neighborhood of 6 at the higher temperatures. As the temperature is lowered, a region is encountered in which the heat capacity falls off rapidly and, in the case of at least one substance (diamond) and probably of many, becomes immeasurably small at temperatures considerably above the absolute zero.

It is apparent that the heat capacity-temperature curves are of the same character. Lewis and Gibson[1] have demonstrated that the atomic heat capacities at constant volume are expressible as functions of the temperature for a large number of substances by the equation

$$C_v = F\left(\frac{T}{\theta}\right)^n,$$

in which F is the same function for all,[2] and θ and n are constants characteristic of the particular substance. The constant, θ, has the dimensions of temperature and may be set equal to the temperature at which $C_v = \frac{3}{2}R = 2.98$ cals. Substances may be divided into two classes with respect to the value of n. For the elements which crystallize in the cubic system, and for thallium, zinc and solid mercury and for the alkali halides as far as investigated, n is equal to unity (Class I). For other substances n has values less than unity,

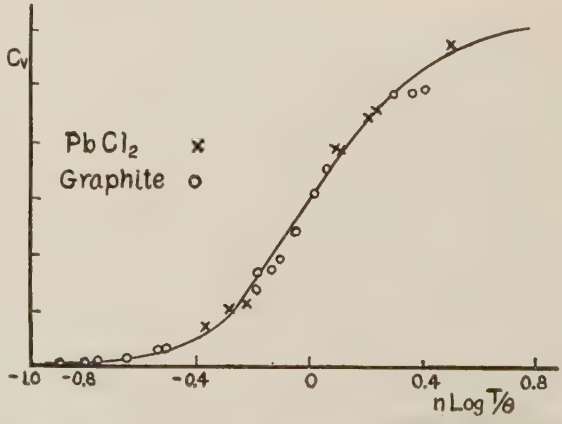


FIG. 10. $C_v - n \log T/\theta$ for Graphite and Lead Chloride

[1] *J. Am. Chem. Soc.*, 39, 2554 (1917).

[2] A discussion of the probable form of this function will be found in Chapter XVII.

ranging from 0.90 for thallous chloride down to 0.31 for solid benzene (Class II).

If the above relation is correct, plots of the value of C_v against $n \log \frac{T}{\theta}$ for different substances should lie on the same curve. Such values have been plotted in Fig. 10 for graphite and lead chloride of Class II. The values of n and θ for different substances which give the same curve as in Fig. 10 are recorded in the following table.

TABLE V

VALUE OF n AND θ

	n	θ	$\log \theta$
Lead	1	22.0	1.342
Diamond	1	461	2.664
Potassium chloride	1	56	1.75
Graphite	0.789	393	2.594
Lead chloride	0.796	45.7	1.660

THE MESOMORPHIC STATE (LIQUID CRYSTALS)

The majority of substances may be obtained in one or more crystalline phases, a liquid phase and a vapor phase only. It appears, however, that a restricted group of organic substances are capable of forming yet another phase intermediate both as to occurrence and as to properties between the crystalline and liquid phases. Substances in this state have been termed "liquid crystals" to indicate their transitional character.

It should be understood that liquid crystals do not combine the properties of the liquid and crystalline states. If our ideas as to the ultimate natures of these states are correct, this would be an obvious impossibility, since in the one state the constituent particles are assumed to be distributed at random and in the other state to be arranged in definite space-patterns of greater or less symmetry, all obeying the one fundamental law of rational indices. The particles obviously cannot be at the same time both in a random arrangement and in a definite geometrical arrangement obeying the law of rational indices. Rather, the properties of liquid crystals indicate that these are intermediate between the two states in the sense that while there may be a primitive arrangement of molecules in one plane or around a common axis, this arrangement is not sufficiently elaborate to permit obedience to the law of rational indices. Since the term "liquid crystals" may lead to misunderstanding of the true nature of substances in this state and since it seemingly subordinates the state to the liquid and the crystalline, whereas it actually possesses its own peculiar characteristics, it has been suggested that this designation be abandoned and the term "mesomorphic state" substituted.[1]

[1] G. Friedel, Annales de Physique [9], 18, 272–474 (1922). This 200-page paper contains the most recent account of the properties (especially the optical properties) of liquid crystals.

As an example of a substance yielding a mesomorphic phase, we may take cholesteryl benzoate, the first of such substances to be discovered. Cholesteryl benzoate, which is a crystalline solid at room temperature, melts sharply at 145.5° to a cloudy, viscous liquid, the mesomorphic phase. This is stable up to 178.5°, at which temperature it undergoes an abrupt transition to a clear mobile liquid. The most striking property of the mesomorphic phase is its bi-refringence. Bi-refringence or double refraction consists in the ability to resolve a beam of incident light into two polarized, refracted beams. When a bi-refringent substance is examined between nicol prisms set at right angles, the normally dark field is lightened. That this is not due to optical activity of the ordinary kind is shown by the fact that there is no position of the analyzing prism at which the field becomes dark again, whereas if the prisms are kept at right angles and rotated together, extinction does occur.

Prior to the discovery of liquid crystals, bi-refringence had been observed in the majority of crystals (all except those of the cubic system) in liquids placed in a strong electrostatic or magnetic field, and in amorphous solids subjected to a mechanical stress. The bi-refringence, moreover, had been successfully ascribed to a lack of symmetry within the substance such that physical properties had different numerical values according as they were measured in one or another direction through it. Such substances are said to be anisotropic. Gases, ordinary liquids and crystals of the cubic system are isotropic, the first two being so because of their complete lack of symmetry and the latter because of their very high symmetry. Mesomorphic substances are obviously not crystalline in the ordinary sense, nor are they under any externally applied stress. To account for their bi-refringence and therefore their anisotropic character, it seems necessary to assume that the molecules of such substances are not distributed at random as in an ordinary fluid but in some regular manner, however primitive the arrangement may be when compared to the arrangement of atoms in crystals.

This assumption of molecular orientation is further borne out by the interesting forms which liquid crystals assume. Perhaps the most extraordinary of these are the so-called graded drops (*les gouttes à gradins*). When a small mass of ethyl para-azoxybenzoate, for example, is fused on a carefully cleaned glass plate or a freshly-cut cleavage surface of mica, it does not wet the surface but draws up into a drop whose upper surface is smooth and perfectly plane and whose edges are graded off into steps. The drop appears to be built up of a pile of planes which, when the drop is touched, glide over one another easily and recall the cleavage planes of crystals. It appears probable that these planes are of molecular dimensions in thickness (about 50 Å.). Their edges are made visible under the microscope by the fact that they are terminated by chains of very fine droplets which are bi-refringent.

Other structures, some of them strongly resembling crystalline forms with edges rounded off, are met with when certain of these substances separate from solution. Ammonium oleate yields such forms, resembling double cones, when it separates from an alcoholic solution. When either ethyl para-azoxy-

benzoate or ammonium oleate is melted on glass so that it wets the surface, it may show a fan-like structure or that of a colony of particles of elliptical or spherical cross section.

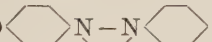
In another group of mesomorphic substances, of which para-azoxyphenetol is an example, filiform (thread) structure is visible. The threads are variable in number, appearing in especially large quantity when the preparation is placed in an electro-static field, in which they orient themselves along the lines of force.

In all the above examples, evidence of a tendency to molecular orientation, producing a structure of some sort, is apparent. It might therefore be expected that the substances would have some effect on X-rays, such as crystals do. Attempts to obtain diffraction effects of this nature have been successful in certain cases—as, for example, that of sodium oleate.[1]

About 250 substances which yield a mesomorphic phase have been prepared up to the present. All are organic compounds having a long straight-chain which may contain para-substituted rings. Examples of the various types are: Ammonium oleate $C_{17}H_{33}COONH_4$,

Ethyl para-azoxybenzoate $C_2H_5CO_2CHCH$ $CHCHCO_2C_2H_5$,

Cholesteryl acetate $CH_3COO.C_{26}H_{43}$,

Para-azoxyphenetol C_2H_5O  OC_2H_5.

For further information on the subject of liquid crystals, the reader is referred to Friedel's paper mentioned above and to "Flussige Krystalle" by Lehmann (Engelmann, Leipzig, 1904) and "Kristallinische Flussigkeiten und Flussige Kristalle" by Schenck (Engelmann, Leipzig, 1905). A recent brief summary appears in Annual Reports of the Progress of Chemistry 1929, p. 22.

[1] de Broglie and Friedel, Compt. rend., 176, 738 (1923)

CHAPTER VI

THERMOCHEMISTRY

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Heat is a form of energy and like all other forms follows the First Law of Thermodynamics which states that the total energy of a closed system remains a constant despite the numerous changes which may be taking place within that system. Historically, the development of Thermochemistry was contemporaneous with that of the doctrine of Conservation of Energy. Thermochemistry treats of the *heat effects* and *internal energy changes* accompanying chemical reactions. We speak of a reaction being either endothermic or exothermic meaning that it takes place with an absorption or evolution of heat.

Quantities of heat are usually expressed in terms of the heat capacity of water for a 1° temperature change. It is only of late years from the work of Rowlands,[1] Griffiths[2] and Callendar and Barnes[3] that it has been realized that the specific heat of water varied with the temperature. Hence, the calorie is only fully defined when the particular degree of temperature is specified through which unit mass of water is heated.

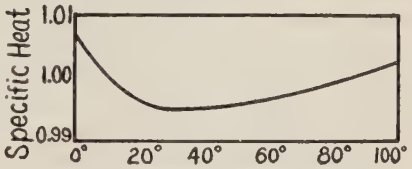

FIG. 1. Specific Heat of Water

Two units have been used to measure amounts of heat, the 15° calorie which is equal to the amount of energy required to raise the temperature of one gram of water from 15° to 16° C. and the mean calorie which is 1/100th part of the amount of energy required to raise one gram of water from 0° to 100° C. Barnes has shown the latter to be larger by 0.017 per cent. The 15° calorie is the one most commonly used. The kilogram calorie is very frequently employed in expressing heats of reaction and is equal to one thousand 15° calories. On account of the interrelation between the various forms of energy, it is quite customary to express a quantity of heat in other units besides the calorie.

The following conversion table will be found useful for practical calculations:

[1] *Proc. Am. Acad.*, Nos. 1880–81.
[2] *Phil. Trans.*, **184**, 361 (1893).
[3] *Proc. Roy. Soc.*, **67**, 238 (1900).

TABLE I

CONVERSION DATA FOR ENERGY QUANTITIES

	Absolute Units	Electrical Units	Heat Units	Mechanical Units
	erg.	joule = watt second	g-calorie	litre-atmosphere
Erg	1	$(10)^{-7}$	$0.02391(10)^{-6}$	$987(10)^{-12}$
Joule	$(10)^{7}$	1	0.2391	0.00987
G. calorie	$4.182(10)^{7}$	4.182	1	0.4130
Litre-atmos.	$1013.3(10)^{6}$	101.3	24.214	1
Horsepower-hour	$26.5(10)^{12}$	$2.65(10)^{6}$	$0.6329(10)^{6}$	26200
R	$83.13(10)^{6}$	8.313	1.9885	0.08204

REACTIONS AT CONSTANT VOLUME AND CONSTANT PRESSURE

When a chemical reaction takes place without volume change, such as the heat of combustion determined in a bomb calorimeter, the increase in the internal energy of the system, ΔU, is called the heat of reaction at constant volume. ΔU for any reaction is defined as the difference between the total internal energy of the resultants and the reactants. Under these conditions no external work is done by the system during the reaction.

In most cases, however, the reaction is carried out at constant pressure and the heat effect measured is slightly different from ΔU. The heat of reaction in a constant pressure calorimeter will be termed ΔH and is defined as the heat absorbed by the reacting system during the reaction. There is a difference in usage regarding the algebraic sign of the heat of reaction. When heat is evolved by our convention, the sign is negative, which corresponds to thermodynamic custom.

In most reactions involving solids or liquids the difference between ΔU and ΔH is negligible, but in cases where gases are concerned, this is not so. Since the heat content of a perfect gas is independent of the pressure, $\Delta H - \Delta U$ must be equal to the work done when the reaction takes place at constant pressure. If the reaction proceeds with the formation of 1 mol. of gas, work has to be done against the external pressure; this can usually be calculated with sufficient accuracy by assuming that the gases obey the law $PV = RT$. ΔH and ΔU measure the heat absorbed in the reaction from the surroundings, and since, if at constant pressure a gas is produced, work is done by the system on the surroundings, an additional quantity of heat equal to the work done must therefore be absorbed.

$$\Delta H = \Delta U + RT. \tag{1}$$

The decrease in energy content of a substance attending any change in state is given by the difference between the heat absorbed and the work done. In general, if Δn is the number of mols. of gas produced by the reaction less the

number consumed, then

$$\Delta H = \Delta U + \Delta nRT. \tag{2}$$

When the result is expressed in calories, $R = 1.9885$. For 18° C.

$$\Delta H = \Delta U + 580\Delta n. \tag{3}$$

The combustion of benzoic acid takes place in accordance with the equation

$$C_6H_5COOH + 15(\tfrac{1}{2}O_2) = 7CO_2 + 3H_2O + 77{,}214 \text{ cals.}$$

For this reaction $n = -\frac{1}{2}$ and at 20° C.

$$\Delta H_{293} = -77{,}214 - \tfrac{1}{2} \times 583,$$
$$= -77{,}505 \text{ cals.}$$

Law of Constant Heat Summation

All the calculations made in thermochemical work are based on the law of the conservation of energy. Any system in a given condition has a definite heat content H determined by the state of the system, and the change in heat content ΔH due to any change in state depends solely on the initial and final states. ΔH is the quantity which is determined in the ordinary constant pressure calorimeter and is called the *heat of reaction.* Hess [1] pointed out that the heat evolved in a chemical reaction is independent of the method by which the reaction is made to take place. This principle is known as Hess' Law of Constant Heat Summation and is readily seen to be a corollary of the law of conservation of energy; Hess, however, did his work at a time when the first law was not generally accepted. It is very useful in calculating heat effects attending chemical changes that are not subject to our methods of calorimetry.

Thermochemical Equations: In order to express changes in heat content of a system due to physical or chemical change at constant temperature and pressure, chemical equations are employed in which the chemical symbols denote the stoichiometrical amounts of the substances involved and also the respective heat contents of these substances.

$$H_2\,(g) + I_2\,(s) = 2HI\,(g); \qquad \Delta H = 12{,}200 \text{ cals.}$$

Here

$$\Delta H = H_{2HI\,(g)} - (H_{H_2\,(g)} + H_{I_2\,(s)}).$$

The state of aggregation is designated in a thermochemical equation by attaching to the formula the letters (s), (l), or (g). If one of the reactants is dissolved in water, this fact is shown by giving the number of mols. of water per mol. of reactant. If sufficient water is present so that further addition produces no appreciable heat effect, the symbol (aq) is written in the equation

$$NH_3\,(aq) + HCl\,(aq) = NH_4Cl\,(aq), \qquad \Delta H = -12{,}300 \text{ cals.}$$

[1] *Pogg. Ann.*, **50**, 385 (1840).

Thermochemical equations may be treated algebraically and added to or subtracted from one another.

$C_2H_4\ (g) + 3O_2\ (g) = 2CO_2\ (g) + 2H_2O\ (l)$; $\Delta H = -342{,}000$ cals. (a)
$2C\ (\text{Graphite}) + 2O_2\ (g) = 2CO_2\ (g)$; $\Delta H = -188{,}000$ cals. (b)
$2H_2\ (g) + O_2\ (g) = 2H_2O\ (l)$; $\Delta H = -136{,}000$ cals. (c)

Adding (b) and (c) and subtracting (a), we have

$2C\ (\text{Graphite}) + 2H_2\ (g) = C_2H_4\ (g)$; $\Delta H = 18{,}000$ cals.

or alternatively

$C_2H_4\ (g) = 2C\ (\text{Graphite}) + 2H_2\ (g)$; $\Delta H = -18{,}000$ cals.

When 24 g. of graphite react with 4 g. of hydrogen to form 28 g. of ethylene gas, 18,000 cals. of heat energy are absorbed.

By this method, ΔH may be calculated for reactions where it is impracticable to make a direct measurement. The results obtained when a considerable number of reactions are combined do not possess a high degree of accuracy, since the absolute error of the final result is the sum of the absolute errors of all the determinations considered and may give a very high percentage error.

Heats of Formation: The absolute heat content of any element is unknown and in thermochemical work we deal only with differences; yet it is convenient, for purposes of tabulation, to adopt a standard reference state for each element so that values can be assigned for the heat content of compounds. The heat content has been taken as zero for all elements in the form stable at room temperature. We then speak of the ΔH of a substance, meaning the increase in heat content when that substance is formed from its elements in their standard state. For C_2H_4, $\Delta H = 18{,}000$ cals.

From a table of heat contents, the heat change in any chemical reaction can be calculated by subtracting the sum of the heat contents of the resultants from that for the reactants.

The following example will show the application of the principles discussed above: To find the heat of formation of sulphuric acid from its elements.

$SO_2\ (g) + \text{aq} = SO_2\ \text{aq}$; $\Delta H = -8{,}000$ cals. (a)
$H_2SO_4\ (l) + \text{aq} = H_2SO_4\ \text{aq}$; $\Delta H = -18{,}000$ cals. (b)
$\frac{1}{2}H_2\ (g) + \frac{1}{2}Cl_2\ (g) = HCl\ (g)$; $\Delta H = -22{,}000$ cals. (c)
$HCl\ (g) + \text{aq} = HCl\ \text{aq}$; $\Delta H = -17{,}300$ cals. (d)
$S\ (s) + O_2\ (g) = SO_2\ (g)$; $\Delta H = -70{,}200$ cals. (e)
$H_2\ (g) + \frac{1}{2}O_2\ (g) = H_2O\ (l)$; $\Delta H = -68{,}400$ cals. (f)
$Cl_2\ (g) + SO_2\ \text{aq} + 2H_2O\ (l) = H_2SO_4\ \text{aq} + 2HCl\ \text{aq}$; $\Delta H = -73{,}900$ cals. (g)
From (c) and (d), $\Delta H_{HCl\ aq} = -39{,}300$ cals. (h)
From (a) and (e), $\Delta H_{SO_2\ aq} = -78{,}200$ cals. (i)
From (f), (g), (h) and (i), $\Delta H_{H_2SO_4\ aq} = -210{,}300$ cals. (k)
From (b) and (k), $\Delta H_{H_2SO_4\ (l)} = -192{,}300$ cals.

Thus, by the use of Hess's law, we have found the heat of formation of 98 g.

sulphuric acid from 2 g. hydrogen, 32 g. sulphur and 64 g. oxygen to be $\Delta H = -192{,}300$ cals. The numerical values of heats of formation are those which will be found listed in tables of physical and chemical constants.

The following table will give the heats of formation of some typical inorganic compounds.

TABLE II

HEATS OF FORMATION OF TYPICAL COMPOUNDS

Reaction	ΔH at $T = 288°$ K.
$\frac{1}{2}H_2\,(g) + \frac{1}{2}Cl_2\,(g) = HCl\,(g)$	− 22,000
$\frac{1}{2}H_2\,(g) + \frac{1}{2}Br_2\,(l) = HBr\,(g)$	− 8,640
$\frac{1}{2}H_2\,(g) + \frac{1}{2}I_2\,(s) = HI\,(g)$	5,930
$\frac{1}{2}H_2\,(g) + \frac{1}{2}F_2\,(g) = HF\,(g)$	− 64,000
$H_2 + S$ (rhombic) $= H_2S\,(g)$	− 5,260
$\frac{1}{2}N_2\,(g) + \frac{3}{2}H_2\,(g) = NH_3\,(g)$	− 10,940
$Si\,(s) + 2H_2\,(g) = SiH_4\,(g)$	12,000
$\frac{1}{2}N_2\,(g) + \frac{3}{2}O_2\,(g) + \frac{1}{2}H_2\,(g) = HNO_3\,(l)$	− 35,340
$Na\,(s) + \frac{1}{2}I_2\,(s) = NaI\,(s)$	− 69,460
$2Na\,(s) + C\,(s) + \frac{3}{2}O_2\,(g) = Na_2CO_3\,(s)$	−270,500
$K\,(s) + \frac{1}{2}I_2\,(s) = KI\,(s)$	− 78,700
$Ca\,(s) + I_2\,(s) = CaI_2\,(s)$	−128,500
$Ag\,(s) + \frac{1}{2}F_2\,(g) = AgF\,(s)$	− 48,700
$Ag\,(s) + \frac{1}{2}Cl_2\,(g) = AgCl\,(s)$	− 30,250
$Ag\,(s) + \frac{1}{2}Br_2\,(l) = AgBr\,(s)$	− 23,840
$Ag\,(s) + \frac{1}{2}I_2\,(s) = AgI\,(s)$	− 14,930
$Pb\,(s) + Cl_2\,(g) = PbCl_2\,(s)$	− 85,670
$Pb\,(s) + Br_2\,(l) = PbBr_2\,(s)$	− 66,260
$Pb\,(s) + I_2\,(s) = PbI_2\,(s)$	− 41,850

METHODS OF CALORIMETRY

Measurements of the heat effects accompanying chemical reactions are made in calorimeters. The essential measurements are the change in temperature of the calorimeter and a calibration to determine its heat capacity. The precision attainable depends on a number of factors involved in the design of the calorimeter and a brief discussion will be given of the more important of these.[1]

Temperature Measurement: Various methods have been employed to measure the temperature changes of calorimeters. The simplest method employs a calibrated Beckman thermometer. The limit in efficiency of mercury-in-glass thermometers is probably about 0.0005°. They must not be altered in reading by tapping, and the thread must not stick. Barry[2] has used a thermometer of this type which had a lag of 30 seconds in taking up the temperature of the liquid when the latter was well stirred. For more refined work use is made of either a resistance thermometer[3] or a thermel.[4] With

[1] For a detailed analysis of the various physical processes involved in the measurement of quantities of heat the reader is referred to a monograph by W. P. White, The Modern Calorimeter, Chemical Catalog Co., Inc., 1928.

[2] *J. Am. Chem. Soc.*, **42**, 1918 (1920).

[3] H. C. Dickinson, *Bull. Bur. Standards*, **11**, 191 (1915).

[4] W. P. White, *J. Am. Chem. Soc.*, **34**, 2292 (1914).

either of these an accuracy of 1 or 2 parts in 10,000 is possible in measuring a temperature interval of 1° C. The measurement of the temperature interval usually sets the limits of precision attainable in properly planned calorimetry.

Stirring of the Calorimetric Liquid: Satisfactory stirring of the calorimetric liquid is very essential and has been neglected by many investigators. For bomb calorimetry a ring stirrer is particularly inefficient. The stirrer should be so designed that it does not cause a temperature rise in excess of 0.001° per minute and for work of great precision the heating should be much lower. The whole mass of liquid in the calorimeter must be circulated so that there are no stagnant portions and there must be a thorough mixing of the different portions of the fluid. Dickinson found, with a screw stirrer, differences of 0°.06 the first minute after the heating current was turned off as compared to 0°.5 with a ring stirrer. The energy dissipated by the screw was also less than that from the ring stirrer. In order to have the stirrer produce heat at a uniform rate it is essential for its speed to remain constant since the rate of heat production varies with the cube of the speed.

Thermal Leakage: Thermal leakage has been responsible for many of the interesting and ingenious devices that have been adapted for precise calorimetry. An accurate knowledge is necessary of the heat which has left the calorimeter during the experiment in order to calculate the *total* temperature change due to the reaction. Newton's law of cooling states that the thermal leakage is proportional to the thermal head, φ, which is the temperature difference between the calorimeter and environment. In order for φ to be definite at any instant the calorimeter and jacket should each be at an entirely uniform temperature. Errors in allowing for the thermal leakage may be due to a number of causes most of which arise from incorrect design; inconstant or too large heat of stirring, uncontrolled evaporation, leakage along metal connections and inaccurate determination of the thermal head due to large lags in reaching equilibrium.

There are two distinct methods employed in calorimetry for successfully controlling thermal leakage; the one consists in keeping the temperature of the outer jacket constant, and the other or adiabatic method [1] in keeping the environment at every instant at the same temperature as the calorimeter. This is done either by electrically heating the outer jacket or by using the heat developed by some chemical reaction such as neutralization. The adiabatic method does not diminish error simply by reducing the magnitude of the thermal leakage loss. It does however permit the use of a large air gap if the calorimeter is closed, with a consequent reduction in the leakage constant of the calorimeter. With rapid changes of temperature, the use of a wide air gap may give rise to convection currents, since the temperature of the jacket always lags behind that of the calorimeter, due to a lag in the thermometer itself and to experimental difficulties. The width of the air space between the calorimeter and jacket is important. Too small an air gap means an insufficient amount of insulation around the calorimeter. The increase of

[1] Richards, Henderson, Frevert, *Z. physik. Chem.*, 59, 532 (1907).

insulation due to widening the gap may be considerable at first but soon reaches a maximum point beyond which the leakage rate increases due to the effect of convection currents. Convection has been the cause of the greatest variations in the thermal leakage and it can be avoided by choosing suitable gap widths.[1] The convection and error due to it increases as the cube of the air gap thickness while conduction losses increase at a rate less than the first power. The minimum total error will be secured by choosing a gap thickness which makes the convection error negligible for the thermal head desired. Shields have been placed in the gap between the calorimeter and jacket and, according to White, their real value consists in cutting down convection and enabling one to use a larger gap. The shield should be made from a good thermal conductor and should be as thin as is feasible mechanically.

The interchange of heat between a calorimeter and its surroundings is practically proportional to the temperature difference, except for effects due to evaporation, convection and radiation. In a well-designed calorimeter four fifths of the heat transfer between the calorimeter and jacket is due to air conduction and convection, one fifth to radiation and a very small amount to evaporation. Richards and Burgess [2] found, with an open calorimeter, that when the temperature of the environment was slightly higher than that of the calorimeter (0.1°), there was, in 20 minutes, a barely noticeable change in the temperature of the calorimeter; but, when it was 0.1° lower, a noticeable cooling took place, probably due to distillation of water from the calorimeter and its condensation on the walls of the jacket. Evaporation is usually the most irregular variable in calorimetry. It may consist in distillation to the chamber wall or from the jacket wall to the calorimeter when the latter is the colder or may be an evaporation of water adsorbed on the calorimeter wall. The simplest method to avoid this variable is to use a close-fitting thin metal cover over the calorimeter to check evaporation completely. It may also be necessary to dry the air in the gap between calorimeter and jacket in order to avoid adsorption and desorption effects.

The loss of heat by the calorimeter can be expressed formally by the expression $w + K\varphi$, where K is the constant of Newton's law of cooling, φ, the thermal head, and w consists mainly of the heat of stirring but also includes all other thermal changes which are independent of the thermal head.

The calculation of the cooling correction [3] can be thought of as essentially a multiplication of the calorimeter temperature by a factor giving the temperature loss per degree. The formula for the temperature loss is

$$\text{t.l.} = \left[V_r + \frac{V_r - V_a}{T_r - T_a}(T_x - T_r) \right] t_x, \qquad (4)$$

where V is rate, t the time and the subscripts denote three periods; x, the experimental, r, the chief or second rating period, a, the anterior rating period.

[1] See W. P. White, The Modern Calorimeter, p. 72, et seq.

[2] *J. Am. Chem. Soc.*, **32**, 431 (1910).

[3] W. P. White, *J. Am. Chem. Soc.*, **48**, 1146 (1926).

The fraction is the leakage factor, the change of rate with change of temperature. In most experimental cases the average values of T_x and T_r are nearly equal since the water in the calorimeter is near the final temperature during most of the experimental period due to the fact that the time required for complete thermal equilibrium is much longer than that in which most of the heat is transferred. Since the multiplier of $\frac{V_r - V_a}{T_r - T_a}$ is small the effect of errors is diminished and it is possible to use a value of the thermal leakage modulus, K, which has been previously determined and thus require only the second rating period with each experiment.

$$\text{t.l.} = [V_r + K(T_x - T_r)]t_x. \tag{5}$$

The temperature loss calculation is thus made up of the directly observed loss $V_r t_x$ and a small quantity calculated from the thermal leakage modulus of the calorimeter.

Vacuum Walled Calorimeter: Vacuum-jacketed vessels make admirable calorimeters in work not involving high precision. The thermal leakage may be small with a vessel of this type and only about 20 per cent of that found with a calorimeter surrounded by air. The vacuum type vessel, also, can receive much cruder treatment. One of the greatest advantages comes from the simplicity of the arrangement and its ease of manipulation. The heat capacity can be determined by supplying a measured amount of electrical energy as in all other forms of calorimetry. A very convenient form of this calorimeter was used by Fischer [1] in his work on silver iodide.

The Dewar vessel has some advantages for precise work but these are not so obvious and the precautions necessary are almost as great as with an air surrounded calorimeter.

Adiabatic Calorimetry: The development of the adiabatic calorimeter to a high degree of precision has been largely the work of T. W. Richards and his students. Dickinson has found by direct determinations that it is possible to obtain the same precision with a calorimeter with constant temperature jacket as with an adiabatic; his results agreed within one part in fifteen thousand. The adiabatic method however is essential for precision when the reaction evolving the heat is slow and the measurement extends over a long period of time. Under these circumstances, the thermal leakage corrections with the constant temperature jacket calorimeter may exceed the thermal quantities to be measured. Barry [2] has made an elaborate study of the various errors influencing protracted measurements and has been able to identify all thermal disturbances likely to cause an error of half a gram-calorie or more in adiabatic calorimetry. A closed calorimeter is essential and the insulating air gaps must be dry. The air gap should be at least 40 mm. wide. For the adiabatic measurement of swift reactions the open calorimeter may be used safely,

[1] *Z. anorg. Chem.*, **78**, 57 (1912).

[2] *J. Am. Chem. Soc.*, **42**, 1917 (1920); **44**, 899 (1922).

provided corrections for thermal disturbances due to evaporation be made from observations before and after the reaction period.

Lipsett, Johnson and Maass [1] have developed an interesting rotating calorimeter which can be used to determine heats of solution. A novel device employed was a radiation thermel to determine differences in temperature between calorimeter and jacket. A difference in temperature of 0.0001° could be detected; the temperature rise was measured by a resistance ther-

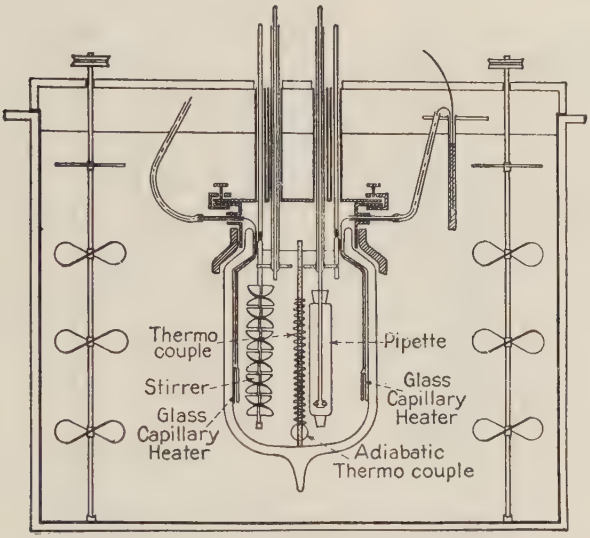

Fig. 2. Differential Adiabatic Calorimeter

mometer in the water jacket. A precision of 0.1 per cent was obtained. By rotating the calorimeter it could be totally enclosed and the only connection with the outside was the axle used for stirring; the calorimeter heated at the rate of 0.0002 per minute due to the rotation. A micro calorimeter was also developed by these workers in which heats of solution could be measured using only 4 c.c. of solvent. The heat capacity of the calorimeter was of the order of 1 gram-calorie. With this device the maximum deviation from the mean was 0.26 per cent.

Lange [2] has described an adiabatic differential calorimeter for measuring extremely small amounts of heats. The arrangement of the calorimeter is shown in Fig. 2. An unsilvered Dewar vessel serves as the calorimeter vessel. It is divided axially in two equal parts by a hard rubber plate which is cemented in position. The middle portion of this plate is removable and serves as the support for a 1000 element iron constantin thermo-element which is well

[1] *J. Am. Chem. Soc.*, **49**, 925, 1940 (1927); **50**, 1030, 2701 (1928).
[2] *Fortschr. der Chem., Phys. und Phys. Chem.*, **19**, Heft 6.

insulated from the medium in which it is to be placed. A sensitivity of $(10)^{-6}$°/mm. on the galvanometer scale was reached which amounts to 0.0009 cal./mm. with a water equivalent for each half of 900 cals. Temperature changes up to $30(10)^{-6}$° were measured directly and larger changes were compensated by electrically heating the cold side. The water tight calorimeter is sunk in a 50 litre bath that can be regulated to a maximum temperature fluctuation of ± 0.0015°. With an asymmetry of 2 per cent between the two halves of the calorimeter an adiabatic error of 0.01° only causes a temperature difference of 10^{-6}°/mm. between the two parts of the calorimeter. The heating and stirring were so effective that within seven seconds after opening the heating circuit the bath temperature was again constant. In one experiment 115 c.c. of 0.002 molar $CaSO_4$ solution was mixed with 700 c.c. of water giving a temperature change of $70(10)^{-6}$°.

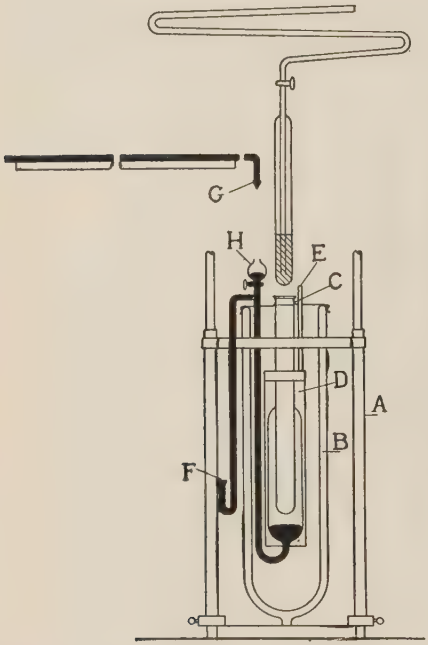

FIG. 3. Ice Calorimeter

Ice Calorimeter: Bunsen[1] was the first to use the decrease in volume when ice melts in order to measure heats of reaction and since his time it has been used by a number of investigators. One of the chief objections to the use of the ice calorimeter for work of precision is the variable density given for ice; Nichols[2] obtained 0.91616 ± 0.00009 while Vincent[3] obtained 0.9160. The trouble seems to arise from an inability to remove all traces of dissolved air; Leduc[4] took extreme precautions to get rid of the last traces of air and found a value of 0.9176. Marshall and Keyes[5] have made an investigation of the heat of absorption of oxygen on charcoal using an ice calorimeter; Ramsay and Shields[6] used it to determine the heat of absorption of hydrogen on platinum black and Foresti[7] determined the heat of absorption of hydrogen on nickel. The calorimeter proper is surrounded by a glass tube

[1] *Pogg. Ann.*, **141**, 1 (1870).
[2] *Phys. Rev.*, **8**, 29 (1899).
[3] *Ibid.*, **15**, 29 (1902).
[4] *Compt. rend.*, **142**, 149 (1906).
[5] *J. Am. Chem. Soc.*, **49**, 156 (1927).
[6] *Z. physik. Chem.*, **25**, 657 (1898).
[7] *Gazz. chim. ital.*, **53**, 487 (1923).

D which is free from liquid and forms an air jacket surrounding the calorimeter. This device [1] is quite effective in cutting down the natural leak of the apparatus. The volume change in the calorimeter is measured by the movement of a mercury column in a horizontal tube. The Boys mantle is surrounded by carefully packed ice contained in a Dewar vessel. With this apparatus a natural leak of 0.02 to 0.04 cm. on the scale per 5 minutes was obtained and this rate remained constant for about 5 hours. The amounts of heat measured by Marshall and Keyes varied from 0.5 to 2.0 small calories and it took about an hour to reach equilibrium in each experiment.

The great advantage of the ice calorimeter is that it can be used to measure very slow reactions with the same accuracy as that obtained in other methods of calorimetry and without so many elaborate accessories. Its most serious limitation is that it can be used only at 0°C.

Continuous Flow Calorimeters: The continuous flow principle of calorimetry which was developed by Callendar and Barnes [2] for measuring specific heat has been more recently used by Keyes [3] for determining heats of neutralization. It can be adapted to any temperature at which thermostats can be successfully operated and an accuracy of 0.1 per cent can be attained. The two liquids which react are led into the mixing calorimeter through coils of silver tubing immersed in a thermostat controlled to 0.001°. The rates of

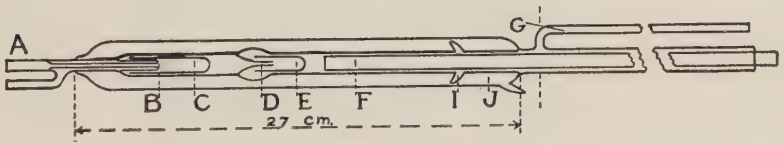

Fig. 4. Continuous Flow Calorimeter

flow are adjusted to give exact neutrality. The liquids enter the calorimeter at *A* and are completely mixed by the baffles *C* and *E* and then pass over the thermometer *F*. The calorimeter is vacuum jacketed and the heat loss varies from 2–6 per cent, depending on the rate of flow. By assuming Newton's Law of Cooling the heat loss can be calculated, and, from a knowledge of the specific heat of the salt solution, a calculation can be made for the heat of neutralization.

The Combustion Bomb: The bomb calorimeter was developed by Berthelot [4] to measure the heats of combustion of organic compounds. Atwater and Snell [5] have modified Berthelot's bomb in some respects, using a gold-plated copper lining in place of platinum. The bomb itself is made of gun metal steel, the cover is heavily threaded and screws down on to a lead washer.

[1] Boys, *Phil. Mag.*, (5) **24**, 214 (1887).
[2] *Trans. Roy. Soc.* (Lond.), **199A**, 55 (1902).
[3] Keyes, Gillespie and Mitsukuri, *J. Am. Chem. Soc.*, **44**, 709 (1922).
[4] *Ann. chim. phys.*, (5) **23**, 160 (1881); (6) **10**, 433 (1887).
[5] *J. Am. Chem. Soc.*, **35**, 659 (1903).

Richards[1] claimed that the lead washer was oxidized during the reaction and he covered it with gold foil to prevent this. By immersing the bomb in an

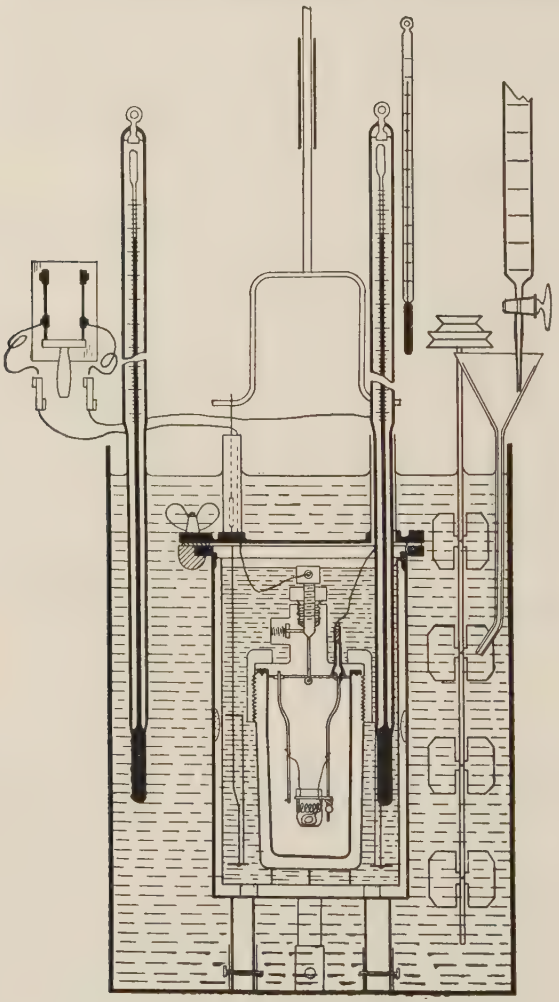

FIG. 5. Combustion Bomb and Calorimeter

adiabatic calorimeter, results were obtained on the combustion of cane sugar with an accuracy of 0.1 per cent. It was necessary to correct for the electrical energy used to heat the wire, the combustion of the iron, and the nitric acid formed by the oxidation of some of the nitrogen contained in the bomb. When liquids are to be used, they are enclosed in glass or collodion bulbs and a known

[1] *Z. physik. Chem.*, **59**, 535 (1907).

amount of sugar is added, which, on ignition, breaks the bulb, volatilizes the liquid and maintains sufficient heat for complete combustion.

Dickinson[1] gives a critical study of combustion calorimetry, using a constant temperature jacket and a platinum resistance thermometer. He includes a complete bibliography on heats of combustion and general calorimetry. Robertson and Garner[2] have developed a calorimeter for determining the heat produced when high explosives are detonated, in order to obtain a measure of the energy developed and also to investigate the nature of the gases evolved. The bomb was made from vanadium steel and the walls and bottom were lined with steel to prevent damage to the bomb from flying fragments. To avoid loss of gas at the instant of explosion the thread of the steel plug was filled with a mixture of litharge and glycerine. The high explosive and detonator were contained in a steel cylinder suspended in the middle of the bomb.

Latent Heat

The *heat of fusion* of solids, the *heat of vaporization* of liquids, and the *heat of transition* of one modification of a solid to another (such as red to yellow phosphorus) are important quantities that are frequently used in calculating heats of reaction and entropy values for pure substances. In nearly every case the transition of the form stable at the lower temperature into that stable at the higher temperature is accompanied by an absorption of heat.

Methods for Determining Latent Heat: A calorimeter of the unstirred type developed in Nernst's laboratory, which depends for its success on the rapid equalization of temperature throughout the calorimeter by means of conduction, has been designed at the Bureau of Standards[3] in connection with an investigation on refrigerants. With this aneroid calorimeter the heat of fusion of ice was determined as 1435.7 cals. per mol. The following table gives the latent heat of fusion of some substances.

TABLE III

Heats of Fusion

Substance	Cals./mol.	Temp.
Sulphur	299.8	115°
Benzene	2368	5.4
Zinc	1840	419
Lead	1214	327
Silver	2273	961
Mercury	565.7	− 39

The heat of fusion is always very much smaller than the heat of vaporization, at least for the elements. A relationship similar to Trouton's Rule exists between the heat of fusion and the melting point.

$$\Delta H \text{ (fusion)} = 2.2 T_{\text{M.P.}} \qquad (6)$$

[1] *Bull. Bur. Standards*, **11**, 189 (1915).
[2] *Proc. Roy. Soc.*, **103A**, 539 (1923).
[3] *Bull. Bur. Standards*, **12**, 23, 49 (1914); **14**, 133 (1918).

TABLE IV

HEAT OF FUSION AND MELTING POINT

Element	ΔH fusion	$T_{M.P.}$	ΔH/T
Ar	268	83.8	3.2
Hg	564	234	2.35
K	625	335	1.87
Na	730	370	1.97
Pb	1150	600	1.92
Zn	1830	691	2.65
Al	2080	930	2.23
Cu	2730	1356	2.02

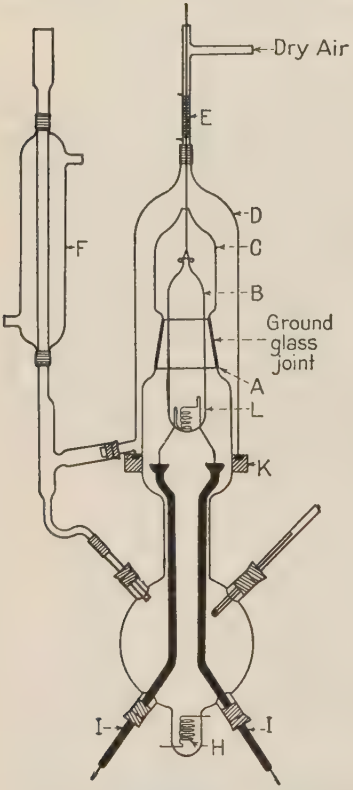

FIG. 6. Calorimeter for Determining Latent Heat of Vaporization

The methods available for determining the heats of vaporization of liquids may be divided into two main classes: (1) condensation methods and (2) evaporation methods. The first method was developed by Berthelot and improved by later workers [1] in this field. One great difficulty with the condensation method is the correction required for the heat given out by the condensed liquid cooling from the boiling temperature to the temperature of the calorimeter. The direct evaporation method does not involve such a correction. Also the heat quantities involved can be determined electrically, which add to the precision of the method. Smith [2] has used this latter method to measure the heat of vaporization of water; Fogler and Rodebush [3] have adapted it for a determination of the heat of vaporization of mercury; more recently Mathews [4] has used it to determine heats of vaporization of a large number of organic compounds. The general method is to evaporate a known weight of material by means of a measured quantity of electrical energy. The vessel *B* in Fig. 6 is suspended from one arm of a balance; the jacket *C* surrounding the vaporizer is kept at the boiling point of the liquid by vapor from the boiler *H*. It is thus possi-

[1] Griffiths, *Phil. Trans.*, **A**, p. 261 (1895) Kahlenberg, *J. Phys. Chem.*, **5**, 215 (1901). Gunther Vogel, *Z. physik. Chem.*, **73**, 445 (1910). Henning, *Ann. Physik.* (4), **21**, 849 (1906).

[2] *Phys. Rev.*, **33**, 173 (1911).

[3] *J. Am. Chem. Soc.*, **45**, 2080 (1923).

[4] *J. Am. Chem. Soc.*, **48**, 562 (1926).

ble to carry out the evaporation adiabatically and there are no heat losses to be taken into account; all the energy supplied to the heater L is used to evaporate liquid.

The following table taken from Mathews work gives the latent heat of vaporization of a number of organic compounds:

TABLE V

HEATS OF VAPORIZATION

Substance	Cals. per g. mol.	Temp. °C.
Benzene	7367	80.20
N-Heptane	7647	97.23
Cyclohexane	7032	80.00
Toluene	7966	109.66
O-Xylene	8797	141.41
Ethyl iodide	7118	71.16
Carbon tetrachloride	7161,	75.40
Carbon bisulfide	6400	45.29
Methyl alcohol	8437	63.81
Ethyl alcohol	9298	77.42
Acetone	7087	56.00
Ethyl ether	6379	33.99
Ethyl acetate	7718	76.00
Bromine	3643	61
Iodine	3039	184
Nitrogen	1334	−195.6
Oxygen	1631	−182.9
Water	9661	
Mercury	14670	
Sodium	24600	
Potassium	20200	
Zinc	29500	
Cadmium	25300	
Lead	45500	

It is also possible to determine heats of vaporization by means of the Clapeyron-Clausius equation from existing data on vapor pressure.

$$\frac{d \ln p}{dT} = -\frac{\Delta H}{RT^2}. \tag{7}$$

This equation assumes that the simple gas laws apply to saturated vapors and that the specific volume in the liquid state is negligible compared to that of the vapor

Fogler and Rodebush determine a value of 14,670 cals. for the latent heat of evaporation of mercury at 298° C. and calculate a value of 14,615 cals. from the vapor pressure data of Smith and Menzies. On account of the difficulties inherent in making direct measurements at high temperatures they prefer to determine the vapor pressures of cadmium at a number of temperatures and calculate the latent heat; this leads to a value of 25,350 cals. per mol at 321° C.

Mathews fits an equation of the form

$$\log p = C + A/T + B/T^2 \tag{8}$$

to the vapor pressure data of some organic compounds; this is differentiated to give the value for dp/dT which in turn is fitted to the Clapeyron equation

$$\frac{\Delta H}{T} = \frac{dp}{dT}(V - v). \tag{9}$$

The results calculated in this manner give good agreement with those measured as evidenced by the data in Table VI.

TABLE VI

HEATS OF VAPORIZATION

Substance	Expt. Value	Calc. Value
Acetone	122.06	120.32
Benzene	94.36	94.68
N-heptane	76.33	78.32

Keyes and Beattie[1] have developed a direct method of determining latent heats of vaporization at temperatures other than the boiling point of the liquid.

Trouton[2] pointed out an interesting relationship between the latent heat of vaporization of a substance and its absolute boiling point.

$$\frac{\Delta H}{T_{\text{B.P.}}} = 21. \tag{10}$$

This rule gives only rough values and when applied to liquids boiling over a wide range, the constant shows a marked trend. Cederberg[3] has derived an equation which enables one to calculate the Trouton coefficients from critical constants. Nernst has derived an equation of state for a saturated vapor of the form

$$p(V - v) = RT\left(1 - \frac{p}{\pi_0}\right) \tag{11}$$

and this combined with the Clapeyron equation gives

$$\frac{\Delta H}{T} = RT\frac{d\ln p}{dT}\left(1 - \frac{p}{\pi_0}\right). \tag{12}$$

By differentiation of the Van der Waals[4] vapor pressure formula

$$\log\frac{p}{\pi_0} = a\left(1 - \frac{\theta_0}{T}\right) \tag{13}$$

[1] *J. Am. Chem. Soc.*, **46**, 1753 (1924).

[2] *Phil. Mag.* (5) **18**, 54 (1884).

[3] *Z. physik. Chem.*, **77**, 498 (1911).

[4] Die Kontinuität des gasförmigen u. flüssigen Zustandes, 2 Aufl. S. 158, Leipzig, g.a Barth 1899.

the equation

$$\frac{d\,ln\,p}{dT} = \frac{ln\frac{\pi_0}{p}}{T\left(1 - \frac{T}{\theta_0}\right)} \tag{14}$$

is obtained. By combining this with equation (12) one obtains

$$\frac{\Delta H_{B.P.}}{T_{B.P.}} = \frac{R\,ln\,\pi_0\left(1 - \frac{1}{\pi_0}\right)}{1 - \frac{T_{B.P.}}{\theta_0}}, \tag{15}$$

where π_0 is expressed in atmospheres. This relationship gives an explanation for Trouton's rule. Guldberg [1] has shown that for a large number of substances the absolute boiling point is approximately 2/3 of the critical temperature; hence the quotient $\frac{T_{B.P.}}{\theta_0}$ should be roughly constant. Deviations from Trouton's rule are to be expected for substances possessing an unusually small or large critical pressure; in general these are the liquefied gases and high boiling substances. Table VII gives some quantitative data calculated from equation (15).

TABLE VII

TROUTON'S CONSTANTS

Substance	$T_{B.P.}$	ΔH	θ_0	π_0	$\frac{\Delta H}{T_{B.P.}}$ (obs.)	$\frac{\Delta H}{T_{B.P.}}$ (calc.)
Helium	4.21	22	5.20	2.26	5.2	4.7
Hydrogen	20.41	216	32.00	11.00	10.6	11.9
Nitrogen	77.25	1333	125.96	33.49	17.3	17.5
Oxygen	90.10	1628	154.25	49.71	18.1	18.3
Ammonia	239.6	5562	406.0	112.30	23.2	22.7
Carbon bisulfide	319.3	6391	546.1	72.87	20.0	20.2
Ethyl formate	327.4	7193	508.4	46.83	22.0	21.0
Methyl acetate	330.2	7267	506.8	46.29	22.0	21.4
Ethyl acetate	350.2	7710	523.2	38.00	22.0	21.3
Ethyl alcohol	351.4	9410	516.2	62.96	26.8	25.4
Methyl propionate	352.8	7718	530.5	39.51	21.9	21.2
Methyl isobutyrate	365.4	7979	540.7	33.88	21.8	20.9
Ethyl propionate	372.1	8178	545.8	33.17	22.0	21.2
Water	373.1	9700	647.1	217.50	26.0	25.1
Aniline	457.0	9655	698.7	52.35	21.1	22.3

Hildebrand [2] showed that $\frac{\Delta H}{T}$ is the same for different substances if they are compared, not at the boiling points, but at temperatures where the liquids

[1] *Z. physik Chem.*, **5**, 374 (1890).

[2] *J. Am. Chem. Soc.*, **37**, 970 (1915).

have the same vapor concentration. The pressure is low enough for the vapor to obey the gas laws.

TABLE VIII

HILDEBRAND'S CONSTANTS FOR $\frac{\Delta H}{T}$

Substance	$\frac{\Delta H}{T}$	Substance	$\frac{\Delta H}{T}$
Nitrogen	27.6	Zinc	26.4
Oxygen	27.6	Ammonia	32.4
Hexane	27.2	Water	32
Stannic chloride	27.2	Ethyl alcohol	33.4
Mercury	26.2		

A few determinations have been made on the heats of transition when a substance passes from one allotropic state to another and the following table gives some of the results obtained.

TABLE IX

HEATS OF TRANSITION

Substance	States	ΔH	
P_2O_5	Crystalline—glassy	−11700 cals.	
P	White—red	− 3700	
HgI_2	Yellow—red	− 3000	
AgBr	Pptd.—crystalline	− 3400	
AgI	Regular—hexagonal	− 1530	
Sn	White—grey	− 591	at 19° C.

SPECIFIC HEAT

The quantity of heat necessary to raise the temperature of 1 g. of a substance through 1° C. at any temperature is called the specific heat of the substance for that temperature.

Variation of Heat of Reaction with Temperature: Each heat of reaction is given for a definite temperature but this does not mean that the temperature has been constant throughout the reaction. In a combustion bomb the temperature may be very high at the moment of the combustion but the final temperature is only a few degrees different from the initial temperature. All we are concerned with is the initial and final state. For the applications of Hess's law, it is necessary for all the heats of reaction concerned to be calculated for a single temperature. Most of the calorimetric data in the literature are for a temperature of about 18° C. It is frequently required to know the heat of some particular reaction at another temperature and this can be readily calculated from a knowledge of the specific heats of the resultants and reactants of the reaction. Let ΔH_1 be the heat of reaction at temperature T_1 and ΔH_2 at T_2. Let us consider the following cyclical process: the reaction is carried out at T_1 with an absorption of heat ΔH_1 and the resultants of the reaction are heated to T_2 whereby an amount of heat $(T_2 - T_1)C''$ is absorbed, where C'' is the mean molal heat capacity of the resultants between T_1 and T_2; again,

let us heat the reactants from T_1 to T_2 with an absorption of heat $(T_2 - T_1)C'$, where C' is the mean molal heat capacity of the reactants, and then carry out the reaction at T_2 with an absorption of heat ΔH_2. Then, by the First Law of Thermodynamics,

$$\Delta H_2 + C'(T_2 - T_1) = \Delta H_1 + C''(T_2 - T_1), \tag{16}$$

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = C'' - C'. \tag{17}$$

When the difference between T_2 and T_1 becomes infinitesimal, this reduces to

$$\left(\frac{d\Delta H}{dT}\right)_p = \Delta C_p, \tag{18}$$

where ΔC_p is the sum of the heat capacities of the resultants less that for the reactants or the total increase in heat capacity from the reaction. This equation was first deduced by Kirchoff.[1] The molal heat capacity of a substance is defined as

$$C_p = \left(\frac{dH}{dT}\right)_p. \tag{19}$$

If it can be regarded as constant, we may define C_p as the heat required to raise one mol. of the substance one degree. If we have a curve plotting H against T for a substance, the tangent at any point will give the molal heat capacity for that particular temperature. Over a small range of temperature around room temperature C_p can be regarded as constant and

$$\Delta H_2 - \Delta H_1 = C_p(T_2 - T_1). \tag{20}$$

For the reaction,

$$2H_2\ (g) + O_2\ (g) = 2H_2O\ (g), \qquad \Delta H_{373}^\circ = -116{,}115 \text{ cals.}$$

The molal heat capacities are as follows:

H_2; $C_p = 6.818$,
O_2; $C_p = 6.960$,
H_2O; $C_p = 9.000$.

Hence, $\Delta C_p = -2.596$. For the interval 100° C. to 130° C.,

$$\Delta H_{403}^\circ - \Delta H_{373}^\circ = -2.596 \times 30 = -77.88 \text{ cals.};$$

hence

$$\Delta H_{403}^\circ = -116{,}193 \text{ cals.}$$

When we are dealing with rapid variations in heat capacity or large temperature ranges, an empirical equation can be set up to express the variation of heat capacity with temperature.

$$C_p = a + bT + cT^2 + \cdots, \tag{21}$$

[1] *Ann. Physik*, (2) **103**, 177 (1858).

where the number of terms will depend on the temperature range and the accuracy of the data. In dealing with a chemical reaction for each of whose members a heat capacity equation has been determined over a range of temperature,

$$\Delta C_p = a_0 + b_0 T + c_0 T^2 + \cdots, \tag{22}$$

where a_0 is the algebraic sum of all the a's, b_0 of all the b's and so on. By the use of this equation we are now in a position to integrate equation (18).

$$\Delta H = \Delta H_0 + a_0 T + \tfrac{1}{2} b_0 T^2 + \tfrac{1}{3} c_0 T^3 + \cdots, \tag{23}$$

where ΔH_0 is an integration constant and can be calculated from a single experiment.

Let us illustrate the usefulness of this method by calculating $\Delta H_{1273}°$ for the reaction

$$H_2\,(g) + \tfrac{1}{2}O_2\,(g) = H_2O\,(g)$$

from the following data:

$$(a) \quad H_2\,(g) + \tfrac{1}{2}O_2\,(g) = H_2O\,(l); \qquad \Delta H_{293} = -68{,}400 \text{ cals.}$$

$$(b) \quad H_2O\,(l) = H_2O\,(g); \qquad \Delta H_{373} = 9670 \text{ cals.}$$

The molal heat capacities at constant pressure of the gases involved are given by the equations:

$$O_2\,(g); \qquad C_p = 6.69 + 0.0007T,$$
$$H_2\,(g); \qquad C_p = 6.54 + 0.0007T,$$
$$H_2O\,(g); \qquad C_p = 8.81 - 0.0019T + 0.00000222T^2.$$

For the reaction, $H_2O\,(l) = H_2O\,(g)$,

$$\Delta C_p = 9.19 - 0.0019T + 0.00000222T^2$$

and

$$\Delta H = \Delta H_0 - 9.19T - 0.00095T^2 + 0.00000074T^3.$$

Whence, at 100° C., $9670 = \Delta H_0 - 3428 - 132 + 38$; hence

$$(c) \quad \Delta H = 13{,}192 - 9.19T - 0.00095T^2 + 0.00000074T^3,$$
$$(d) \quad \Delta H_{293}° = 10{,}439.$$

Now, summing (a) and (d),

$$H_2\,(g) + \tfrac{1}{2}O_2\,(g) = H_2O\,(g), \qquad \Delta H_{293} = -57{,}961,$$

and

$$\Delta C_p = -1.08 - 0.0029T + 0.00000222T^2,$$

and

$$\Delta H = -57{,}539 - 1.08T - 0.00145T^2 + 0.00000074T^3;$$

hence

$$\Delta H_{1273}° = -59{,}738 \text{ cals.}$$

Specific Heat of Gases: In treating gases there are three quantities which are of practical and theoretical significance: c_v, the *specific heat at constant volume*, c_p, the *specific heat at constant pressure*, and γ the ratio of these two quantities. By multiplying the specific heats by M, the molecular weight, the Molecular Heats C_p and C_v are obtained. To show the relationship of these quantities to one another it is convenient to assume that we are dealing

with an ideal gas. Boyle's law holds and the internal energy of the gas is independent of its volume,

$$\left(\frac{\partial U}{\partial v}\right)_T = 0. \tag{24}$$

If one gram. mol. of a substance is heated from temperature T to $T + dT$ at constant pressure the amount of heat consumed by definition is $C_p \cdot dT$. It is possible to consider the heating as accomplished in another manner; the substance may first be heated at constant volume with an expenditure of heat $C_v \cdot dT$ and then allowed to expand at constant temperature to the original pressure. This last process requires an amount of heat $\left(\frac{\partial U}{\partial v}\right)_T \partial v + p dv$. Hence,

$$C_p dT = C_v dT + \left\{ p + \left(\frac{\partial U}{\partial v}\right)_T \right\} dv \tag{25}$$

or

$$C_p - C_v = \left\{ p + \left(\frac{\partial U}{\partial v}\right)_T \right\} \frac{\partial v}{\partial T}. \tag{26}$$

or, since we are dealing with a perfect gas,

$$C_p - C_v = p \frac{dv}{dT} = R.$$

The heat content of a mol. of gas is the sum of the energy of thermal agitation of the molecules and the energy of other types of motion within the molecule. If we designate with E the increase in the last named types per degree rise in temperature then

$$C_v = \tfrac{1}{2} M \frac{\mu^2}{T} + E, \tag{27}$$

where M is the molecular weight and μ the velocity of the molecule and since

$$\frac{pv}{T} = R = \frac{1}{3} \frac{M\mu^2}{T}$$

$$C_p = \tfrac{1}{2} M \frac{\mu^2}{T} + \frac{1}{3} \frac{M\mu^2}{T} + E = \frac{5}{6} \frac{M\mu^2}{T} + E$$

and

$$\frac{C_p}{C_v} = \frac{\frac{5}{6} \frac{M\mu^2}{T} + E}{\frac{1}{2} \frac{M\mu^2}{T} + E}. \tag{28}$$

From this equation it follows that γ must always be smaller than 1.667 since E of necessity has a positive value and that 1.667 is the limiting value

when E is very small. The ratio approaches unity when E is very large. The following table shows that this range of values is correct.

TABLE X

Ratio of Specific Heats

Gas	γ
Mercury	1.666
Oxygen	1.398
Chlorine	1.32
Carbon dioxide	1.300
Ethyl ether	1.06

Monatomic gases appear to possess only translational energy in virtue of the thermal agitation of the system and the equipartition principle of statistical mechanics gives a satisfactory explanation of the observed specific heat. For polyatomic molecules it is necessary to take into account both rotational and vibrational energy in order to explain the experimental data and these energies are not amenable to classical mechanics and must be treated by the quantum theory.

Eucken [1] has determined the specific heat of hydrogen at low temperatures. The hydrogen was contained in a thin walled steel vessel. The method was similar to that used by Nernst in determining the specific heat of solids. At the temperatures employed the heat capacity of the container was very small in comparison to that of the gas and thus a higher degree of accuracy was attainable. Eucken found the following values for hydrogen:

Molecular Heat of Hydrogen

$T°$ abs.	C_v	$C_{\text{rotational}}$
35	2.98	0.00
40	2.98	0.00
45	3.00	0.02
50	3.01	0.03
60	2.99	0.01
65	3.04	0.06
70	3.10	0.12
80	3.14	0.16
85	3.21	0.23
90	3.26	0.28
100	3.42	0.44
110	3.62	0.64
196.5	4.39	1.41
273.1	4.94	1.96

Hund [2] has treated the specific heat of the hydrogen molecule on the basis of the wave mechanics. Dennison [3] has extended this treatment and been able to account theoretically for Eucken's observed results by assuming that

[1] *Sitz.-ber. preuss. Akad. Wiss.*, 144 (1912).
[2] *Z. f. Physik.*, **42**, 93 (1927).
[3] *Proc. Roy. Soc.*, **115**, 483 (1927).

there are symmetrical and anti-symmetrical rotational states of the hydrogen molecule and that the time of transition between the two is very long compared to the time of the experiment. Bonhoeffer and Harteck [1] have been able to demonstrate experimentally the presence of these two forms of hydrogen.

According to Dennison the rotational specific heat of hydrogen is given by the formula

$$C_r = Rx^2 \frac{d^2 \ln Q}{dx^2},$$

for parahydrogen

$$Q_P = e^{-(x/4)} + 5e^{-(5/2)x^2} + 9e^{-(9/2)x^2},$$

and for orthohydrogen

$$Q_O = 3e^{-(3/2)x^2} + 7e^{-(7/2)x^2} + 11e^{-(11/2)x^2},$$

where

$$x = \frac{h^2}{8\pi^2 JkT},$$

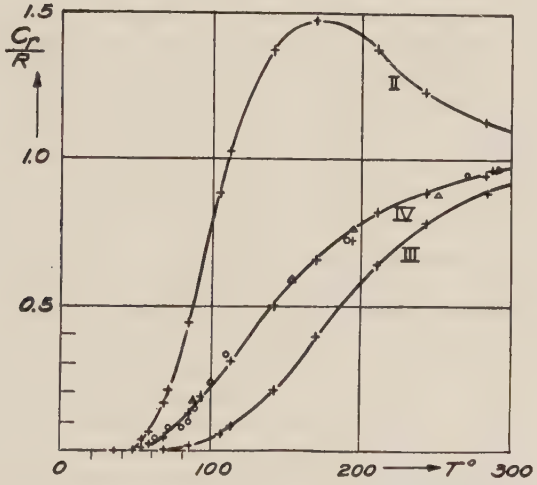

Fig. 6a. Rotational Specific Heat of Hydrogen. II theoretical curve for parahydrogen III theoretical curve for orthohydrogen. IV calculated curve for a mixture of 1 part para and 3 parts ortho. The points on this curve are taken from experiment.

and J is the moment of inertia of the molecule. The accompanying Figure 6A shows the nature of the calculated results. Eucken, Hiller and Clusius [2] have determined experimentally the specific heat of a 95 per cent parahydrogen and the table gives the results obtained.

[1] *Berl. Ber.*, 1929, 103.
[2] *Z. physik. Chem.*, (B), **4**, 142 (1929).

Specific Heat of Para Hydrogen

T	C_v (calc.)	C_v (obs.)
83.88	0.750	0.897
89.50	0.955	1.037
95.31	1.192	1.203
100.98	1.405	1.443
106.62	1.652	1.675
112.42	1.856	1.836
117.97	2.053	2.118
123.49	2.208	2.286
129.50	2.366	2.342
135.33	2.491	2.457
141.53	2.608	2.570
147.19	2.683	2.714
154.43	2.743	2.629
161.18	2.785	2.792

Determination of Molecular Heat at Constant Pressure: The difficulty in determining accurately the specific heats of gases is due to the fact that the mass of a given volume is relatively small. Two general methods have been adopted, (1) The method of mixtures, (2) The constant flow method. Delaroche and Berard [1] first used the method of mixtures whereby a known volume of gas heated to a definite temperature is passed through a calorimeter and the heat liberated is measured. Regnault [2] elaborated the method paying great attention to details and was the first to obtain reliable data. Wiedemann [3] further improved the calorimeter by decreasing its size and obtaining a more rapid heat exchange between the gas and the calorimeter. A known volume of gas is passed through a tube packed with copper filings which is immersed in a constant temperature bath at temperature T_2. From here it passes to silver tubes packed with silver turnings in the calorimeter and leaves the calorimeter at temperature T. Then

$$C_p = \frac{wtM}{M(T_2 - T)}, \tag{29}$$

where t = rise in temperature of calorimeter, w = water equivalent of calorimeter, M = weight of gas passed.

Holborn and Henning [4] have used the same method to determine the specific heat of air, nitrogen and carbon dioxide up to 1400° C. The following table gives the specific heat of air at varying temperatures by several observers.

[1] *Ann. Chim.*, **85**, 72 (1813).
[2] *Memoires de l'Institute de France*, **26**, 1862.
[3] Pogg. Ann., **157**, 1 (1876).
[4] *Ann. Physik*, **23**, 809 (1907).

TABLE XI

SPECIFIC HEAT OF AIR

° C.	Regnault	Wiedemann	Holborn and Austin
0	0.1870	0.1952	0.2028
100	0.2145	0.2169	0.2161
200	0.2396	0.2387	0.2285
400	—	—	0.2502
600	—	—	0.2678
800	—	—	0.2815

McCollum [1] has described a calorimeter in which a cooled gas is passed through the calorimeter and the cooling effect offset by a measured input of electrical energy. In this way it was unnecessary to measure either temperature change or the water equivalent of the calorimeter.

A method already mentioned, due to Callendar, has been developed by Scheel and Heuse [2] which gives the specific heat over a very small temperature interval. The gas at a definite temperature flows into the calorimeter, is heated electrically and the rise in temperature measured by a resistance thermometer.

If i is the current, E the potential difference across the heating coil, dT the rise in temperature of the gas, Q the rate of flow of gas in grams per second, J the mechanical equivalent of heat and c_p the specific heat of the gas, then

$$Ei = Jc_pQdT + hdT, \tag{30}$$

where hdT is a term representing the heat losses. By experimenting with two rates of flow and adjusting the current to keep dT constant, the second term can be eliminated and c_p determined directly.

Molecular Heats of Gases at Constant Volume: Joly [3] has developed a method for determining specific heats of gases at constant volume; a metal vessel is suspended from a balance in a cavity through which a rapid current of steam can be admitted and its weight is determined. Steam is admitted and condenses on the cold vessel until it is heated to 100° C. Since the whole space is filled with steam, there is no heat loss and the amount of water condensed is a measure of the heat necessary to bring the vessel from its initial temperature to 100° C. If the vessel is first evacuated and then filled with gas, the difference between the two increments gives directly the quantity of heat necessary to heat the enclosed gas to 100° C.

The Explosion Method: Bunsen, in 1867, first used the explosion method for determining specific heats at high temperatures. The combustible gas and

[1] *J. Am. Chem. Soc.*, **49**, 28 (1927).
[2] *Ann. Physik.*, **37**, 79 (1812).
[3] *Phil. Trans.*, **182**, 73 (1892).

oxygen are mixed with various indifferent gases, exploded in a closed bomb and the maximum pressure of the explosion measured. From this, one can calculate the maximum temperature attained and hence the heat capacity of the gaseous mixture, since the heat of reaction is known. Pier[1] and Bjerrum[2] have been recent workers in this field. Pier showed that previous workers had failed to measure the maximum pressure developed in the explosion and he developed a manometer that was practically free from inertia and gave the pressure reading in less than 1/100 sec. It consisted of a corrugated steel membrane of 0.1 mm. thickness fastened over a 3 cm. hole in the explosion bomb. A mirror was attached directly to the membrane and its movement was recorded by a beam of light reflected to a moving film. The chief source of uncertainty in results of explosion experiments since the introduction of this manometer lies in the estimation of the heat loss while the maximum pressure is being attained. Wohl[3] states that by using a bomb with enamelled walls the heat losses cause an error of the order of 0.4 per cent in determining the maximum temperature of the explosion. From the maximum pressure P of the explosion, the temperature can be calculated by the equation

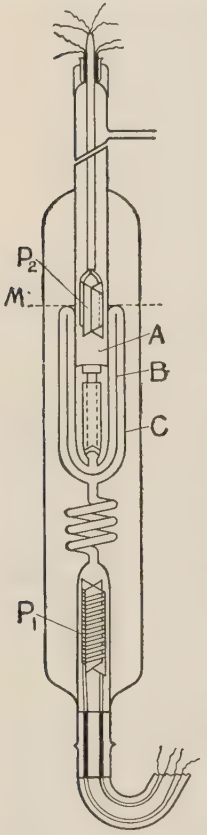

Fig. 7. Continuous Flow Calorimeter for Determining Specific Heat

$$\frac{T_2}{T_1} = \frac{P}{p \cdot \epsilon}, \tag{31}$$

where T_1 and T_2 are the initial and final temperatures, p the initial pressure, and ϵ the ratio of the number of molecules before to that after the explosion. Pier found, between 0° and 2350° C., $C_v = 2.977$ for argon. In the following table, the molecular heats at constant volume of a few gases are given. This method has proved of value not only in the direct determination of specific heat but also in determining the heats of dissociation of a number of substances. Wohl has determined the heats of dissociation of hydrogen and chlorine from the explosion of mixtures of hydrogen and chlorine and obtained a value of 97,000 cals. for hydrogen and 57,000 cals. for chlorine. These values agree well with those obtained from other methods of investigation.

Trautz and Hebbel[4] have extended a method previously developed by Trautz and Grosskinsky in which a small portion of the gas in the interior of

[1] *Z. Elektrochem.*, **15**, 537 (1909); **16**, 897 (1910).
[2] *Z. physik. Chem.*, **79**, 513 (1912); **87**, 641 (1914).
[3] *Z. Electrochem.*, **30**, 36 (1924).
[4] *Ann. Physik*, **74**, 285 (1924).

a body of gas is given a quantity of heat of the order of 0.02 cal. in about 0.2 secs. The change in pressure thus produced is measured before any of the heated gas reaches the walls of the vessel. By this method it is possible to measure the specific heat at a single temperature. The results obtained agree within about 1 per cent with those of Scheel and Heuse.

TABLE XII

C_v FOR SEVERAL GASES

Gas	Temp. in ° C.					
	0°	100°	200°	500°	1200°	2000°
Argon	2.98	2.98	2.98	2.98	3.0	3.0
N_2, O_2, HCl, CO	4.90	4.93	5.17	5.35	5.75	6.22
Cl_2	5.85	5.88	6.12	6.30	6.9	7.4
CO_2, SO_2	6.80	7.43	8.53	9.43	11.1	11.5
$(C_2H_5)_2O$	32	32.6	41.6			

Indirect Methods for C_v: Since the direct determination of C_v for gases is very troublesome, several indirect methods have been worked out that give satisfactory results. The ratio of $\frac{C_p}{C_v}$ can be determined directly and several methods of attack have been employed.

Method of Clément and Désormes:[1] The gas under consideration is placed in a large container at a pressure P_1 which is slightly greater than atmospheric. The container is opened for a moment so that the internal pressure drops to atmospheric and then is quickly closed. While the gas in the container was expanding, it cooled slightly and on warming again the pressure increased to P_2. Let $P_1 = P + p_1$ and $P_2 = P + p_2$, where P is atmospheric pressure and p_1 and p_2 are small compared to P. If V is the volume of the container, then the amount of work done by the escaping gas is $V(p_1 - p_2)$. This work was done at the expense of the heat content of the gas, since we assume that the expansion takes place adiabatically. The amount $t°$ which the gas cooled during expansion can be calculated from the equation

$$\frac{t}{T} = \frac{p_2}{P}, \tag{32}$$

since the pressure rose from P to $P + p_2$, while the temperature changed from $T - t$ to T. The heating is done at constant volume so that the amount of heat consumed is

$$nC_v t = \frac{PV}{RT} C_v t = \frac{p_2 V}{R} C_v. \tag{33}$$

[1] *Jour. de Phys.*, 89, 321, 428 (1819).

Since this quantity is equivalent to the work done by the gas on expansion,

$$p_1 - p_2 = \frac{p_2}{R} C_v. \tag{34}$$

But we have shown that

$$C_p - C_v = R,$$

so

$$\frac{C_p}{C_v} = \frac{p_1}{p_1 - p_2} = \gamma. \tag{35}$$

By working with a large volume of gas and a small pressure difference, it is possible to minimize very greatly the loss of heat due to conduction during the expansion; the chief difficulty is in securing a quick equalization of pressure.

A somewhat better method is due to Lummer and Pringsheim.[1] They filled a vessel of 90 liters capacity with a gas at known temperature and at a pressure which exceeded atmospheric. The excess pressure was allowed to blow off through a large orifice and a complete equalization with atmospheric pressure was ensured. The temperature of the gas was now determined again quickly by a platinum resistance thermometer of very fine wire placed in the center of the flask. Since the process is adiabatic,

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{(\gamma-1)/\gamma}. \tag{36}$$

Subsequent improvements in experimental technique have made this method quite reliable for exact work.

The Method of the Velocity of Sound Waves: This method depends on measurements of the velocity of sound in gases. The velocity of transmission of sound U in any gas is given by the expression

$$U = \sqrt{\frac{p}{d}\gamma}, \tag{37}$$

where d is the density of the gas.

The ratio of the velocity in two gases, both at the same pressure, is

$$\frac{U_1}{U_2} = \sqrt{\frac{\gamma_1 d_2}{\gamma_2 d_1}} \tag{38}$$

or, since, at constant temperature, the densities are proportional to the molecular weights,

$$\frac{U_1}{U_2} = \sqrt{\frac{\gamma_1 M_2}{\gamma_2 M_1}}. \tag{39}$$

[1] *Wied. Ann.*, **64**, 582 (1898).

The ratio of the velocity of sound in any two gases can be determined very accurately by a method developed by Kundt.[1]

FIG. 8. Kundt's Tube for Measuring Velocity of Sound in a Gas

Sound waves are set up in a tube G about 1 metre long and 3–4 cm. in diameter. The tube contains some light powder such as lycopodium. One end of the large tube contains a closely fitting piston A—and the other a loosely fitting piston B and a sounding rod D which is tightly clamped at its centre. By stroking, the rod is caused to vibrate and the dust in the tube is caught up by the vibrating gas and deposited in the positions of least motion. When the gas is tuned by adjusting the position of B the powder collects in tiny heaps at the position of each node in the gas. The distance between two nodes is half the length of the sound wave in the gas.

The value for γ in air has been found to be 1.403. When l for air has been determined by this method, it is possible to determine γ for any gas.

$$\gamma = 1.403 \frac{Ml_1^2}{29.0l_2^2}, \tag{40}$$

where l_1 and l_2 are the nodal distances for the gas and for air under the same conditions of temperature and pressure.

This method has been used to determine the effect of temperature and pressure on C_v for a number of gases. In the temperature range 0–1000° C. the results given in Table XIII have been obtained

TABLE XIII

MOLECULAR HEATS IN CALS./G. MOL.

Gas	C_v	C_p
Air	$4.862+0.00029T+0.0_756T^2$	$6.857+0.000276T+0.0_763T^2$
Nitrogen	$4.820+0.00033T+0.0_747T^2$	$6.815+0.000317T+0.0_753T^2$
Oxygen	$4.982+0.00021T+0.0_755T^2$	$6.980+0.000188T+0.0_767T^2$
Carbon dioxide	$5.582+0.00424T-0.0_6715T^2$	$7.686+0.0040T \quad -0.0_654T^2$

Koch [2] has modified the original Kundt apparatus to work at high pressures and has shown that the value of γ increases with increasing pressure. His results are shown in Table XIV.

[1] *Pogg. Ann.*, **127**, 497 (1866); **135**, 337, 527 (1868).
[2] Sitz. Kgl. Bayer Akad., p. 213, 1913.

TABLE XIV

EFFECT OF PRESSURE ON VALUES OF γ FOR AIR

p in atm.	0°C	−79.3°C
1	1.405	1.405
25	1.473	1.569
50	1.530	1.767
75	1.593	2.001
100	1.646	2.200
125	1.690	2.402
150	1.739	2.469
175	1.783	2.413
200	1.828	2.333

A critical discussion of the methods and results of specific heat measurements in gases will be found in Partington and Shilling.[1]

Specific Heat of Liquids: The specific heats of liquids and solutions have been determined with the aid of the continuous flow method of Callendar and Barnes and also by measuring the heat rise in a Dewar vessel when the system is heated electrically. The difficulty of the latter method is in determining the heat capacity of the calorimeter. Williams and Daniels [2] have measured the specific heat of a number of organic liquids using the Richards adiabatic method of calorimetry. Experiments were made in the range 25–80° C. and it was found that the majority of liquids have specific heats which increase regularly, being a linear function of the temperature. Those liquids not giving straight lines are the ones normally considered as associated where energy is absorbed to cause depolymerization as well as to increase the temperature. Some of the results are given in Table XV.

TABLE XV

EMPIRICAL EQUATIONS FOR C_p

Benzene	$0.3824+0.0_3655t+0.0_585t^2$
Toluene	$0.3726+0.0_3846t$
O-xylene	$0.3874+0.0_3775t$
M-xylene	$0.3764+0.0_3812t$
P-xylene	$0.3695+0.0_393t$
Ethyl alcohol	$0.5068+0.00286t+0.0_554t^2$
Chloroform	$0.2250+0.0_3304t$
Heptane	$0.4755+0.00142t$

Richards and Rowe [3] have measured the specific heat of hydrochloric acid solutions using an adiabatic calorimeter. Richard and Gucker [4] have applied the adiabatic principle to Joule's twin-calorimeter and used it as a precise method for determining specific heats of solutions. The results are accurate

[1] The Specific Heat of Gases, Ernest Benn, Ltd., London, 1924.
[2] *J. Am. Chem. Soc.*, **46**, 904 (1924).
[3] *J. Am. Chem. Soc.*, **42**, 1621 (1920).
[4] *J. Am. Chem. Soc.*, **47**, 1876 (1925).

to about one part in ten thousand. Table XVI gives a comparison with the results of other observers.

TABLE XVI

Specific Heats at 18°C.

	Thomsen	deMarignac	Others	Richards and Rowe	Richards and Gucker
$NaCl \cdot 25H_2O$	0.882	0.876	0.875	0.8776	0.8778
$KNO_3 \cdot 25H_2O$	.832	.831	——	.8321	.8328
$NaNO_3 \cdot 25H_2O$	.863	.868	——	.8695	.8684
$HC_2H_3O_2 \cdot 25H_2O$	——	——	.946	——	.9546
$NaC_2H_3O_2 \cdot 25H_2O$	.872	.9004	——	——	.9010
$H_2C_4H_4O_6 \cdot 25H_2O$	.856	——	.844	——	.8533
$NaOH \cdot 25H_2O$	.909	——	——	——	.9132

Goodwin and Kalmus [1] have measured the specific heats of a number of inorganic salts at a temperature just above their melting point.

TABLE XVII

Molar Heat Capacities of Fused Salts.

Salt	T° C.	C_p
KNO_3	308	33.7
$NaNO_3$	333	36.6
$AgNO_3$	250	26.9
$AgCl$	455	18.5
$AgBr$	430	14.3
$PbCl_2$	498	33.7
$PbBr_2$	488	28.6

In the case of liquid sulphur, Lewis and Randall [2] observed a great rise at 160° C., which they accounted for as due to the transition from S_λ to S_μ.

TABLE XVIII

Specific Heat of Liquid Sulphur

Temp.	c_p	Temp.	c_p
100° C.	0.23	200° C.	0.27
140	0.25	300	0.27
160	0.45	400	0.28
180	0.28		

Dixon and Rodebush [3] have developed the technique for applying an indirect method proposed by Lewis. The pressure on a liquid is changed

[1] *Phys. Rev.*, **28**, 1 (1909).
[2] *J. Am. Chem. Soc.*, **33**, 476 (1911).
[3] *J. Am. Chem. Soc.*, **49**, 1162 (1927).

suddenly and the corresponding change in temperature noted by means of a thermocouple. With proper conditions the entropy remains constant and we have

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{T}{C_p}\right)\left(\frac{\partial V}{\partial T}\right)_p.$$

The thermal expansion data can be obtained from the literature and it is thus possible to calculate C_p. The method was tested with molten metals and proved thoroughly feasible. It should prove a very simple method for obtaining specific heats of organic liquids with an accuracy of better than 1 per cent.

Schulze [1] gives data for a large number of liquids to support a conclusion that $M(C_p - C_v)$ ranges from 10–11 for non-associated liquids and has values ranging from 0 to 10 for alcohols and organic acids which are taken as being associated.

There is generally a considerable deviation from the law of mixtures in calculating the specific heat of mixtures of liquids from that of the individual components. Williams and Daniels [2] have measured the specific heat of a number of binary mixtures. It is evident from their results that the processes taking place on mixing are quite intricate; there is likely a dissociation of the associated molecules of the liquids and some combination between the molecules of the two liquids. The systems benzene-toluene and chloroform-carbon tetrachloride are nearly ideal, but chloroform-acetone varies widely from the ideal condition.

Specific Heat of Solids: The study of the specific heat of solids has proven a particularly fruitful field of endeavor. The law discovered by Dulong and Petit in 1819 was of great value in fixing atomic weights of a number of elements in the early days of atomic weight determinations. It stated that the product of the atomic weight and the specific heat was a constant equal to about 6.4. It held approximately for most of the elements if the values taken were the specific heats at ordinary temperatures. The law however is not at all rigid and some surprising exceptions were found amongst elements of low atomic weight and small atomic volume; Boron 2.6; carbon 2.0; silicon 4.0; beryllium 3.7. Boltzmann has deduced from classical kinetic theory that the value of C_v for elements should be equal to $3R = 5.97$ cals. per degree. Lewis [3] has calculated the value of C_v for all the elements for which accurate data are available from the equation

$$C_p - C_v = \frac{\alpha^2 V T}{\beta} \tag{41}$$

[1] *Physik. Z.*, **26**, 153 (1925).
[2] *J. Am. Chem. Soc.*, **47**, 1490 (1925).
[3] *J. Am. Chem. Soc.*, **29**, 1165, 1516 (1907).

where

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p, \text{ the coefficient of thermal expansion,}$$

$$\beta = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \text{ the coefficient of compressibility,}$$

v = molal volume.

He finds that within the limits of experimental error at 20° C. the atomic heat at constant volume is the same for all solid elements of atomic weight greater than potassium.

Kopp[1] showed that the molecular heat of a compound could be calculated roughly by summing up the specific heats of the individual atoms making up the molecule. The atomic heats of the lighter solid elements and the gases had to be given special values, different from 6.4. The values assigned were:

O	H	F	B	C	Si	S	P
4.0	2.3	5.0	2.7	1.8	3.8	5.4	5.4

Quite good agreement with experimental data has been obtained in hundreds of cases where the calculations have been made.

The exceptions to Dulong and Petit's law have been cleared up by a study of the effect of temperature on specific heat. From the low temperature studies made during the past two decades there has been obtained added support for the quantum theory and much of the experimental evidence supporting the Third Law of Thermodynamics. The following table gives the values of C_v obtained with a number of elements:

TABLE XIX

Atomic Heats at Low Temperatures

	° K.	C_p		° K.	C_p		° K.	C_p
Silver.....	34	1.58	Copper.....	33.4	0.54	Lead.....	23	2.96
	85	4.42		88	3.38		80	5.72
	120	5.20		120	4.58		120	5.93
	200	5.78		200	5.44		200	6.10
	280	6.01		280	5.80		280	6.28
	360	6.21		360	6.02		360	6.45

As the temperature approaches absolute zero the specific heat of all solid bodies approaches zero. As the temperature is increased the specific heat rises, approaching finally, at sufficiently high temperatures, the value required by Dulong and Petit's rule. Einstein[2] has been able to elucidate qualitatively

[1] *Lieb. Ann. Supplement*, 3, 289 (1864).

[2] *Ann. Physik*, [4] 22, 180 (1907).

the variation of the specific heat of solids with temperatures on the basis of the quantum theory and Debye,[1] by an amplification of Einstein's theory, has been able to account quantitatively for the experimental results.

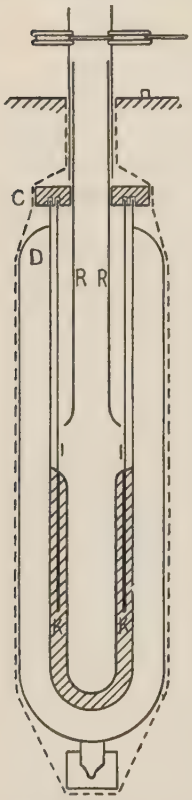

Fig. 9. Copper Calorimeter for Specific Heat

A large amount of work has been done on the variation of the specific heat of solids with temperature at low temperatures and Nernst [2] has given a fairly complete account of this work.

The Copper Calorimeter: The copper calorimeter was developed first by Nernst, Koref, and Lindemann.[3] It works on the principle of a mixing calorimeter with a well-insulated copper block K in a Dewar vessel serving as the calorimeter. Temperature changes are measured by thermoelements I; one end of each is placed in the copper block K, the other in the copper cover C. The whole apparatus is covered with a thin copper sheeting and immersed in a constant temperature bath. The substance whose specific heat is desired is introduced at a known temperature through the tube R and the temperature change determined. Koref[4] has made a number of determinations, using this method. He finds that it works quickly and accurately with a properly constructed calorimeter and that, for determining small amounts of energy, it is preferable to the ice calorimeter. Magnus [5] has used the same method for determining specific heats up to 730° C., employing a large copper block so that his percentage heat losses were smaller. The method, however, only gives average specific heats over a range of temperature.

The Vacuum Calorimeter: The principle of the vacuum calorimeter is that the substance itself serves as the calorimeter; a measured quantity of heat energy is supplied and the temperature rise measured. Several forms of this calorimeter have been developed for low temperature work.[6] In the usual form, the same wire is used for heater and resistance thermometer; at liquid hydrogen temperatures this has proved impracticable so that Schwer used a thermoelement. Gibson and Giaque [7] have used this method and modified the calorimeter slightly.

[1] *Ann. Physik*, [4] **39**, 789 (1912).

[2] Grundlagen des neuen Wärmesatzes, Knapp, 1918. See also T. Estreicher, Sammlung Chem. Vortrage, **20**, 353 (1914); also, Chapter XVII.

[3] *Sitz.-ber. preuss. Akad. Wiss.*, 247 (1910).

[4] *Ann. Physik*, **36**, 49 (1911).

[5] *Physik. Z.*, **14**, 5 (1913).

[6] Eucken, *Physik. Z.*, **10**, 586 (1909). Pollitzer, *Z. Elektrochem.*, **17**, 5 (1911). Nernst and Schwers, *Sitz.-ber. preuss. Akad. Wiss.*, 355 (1914).

[7] *J. Am. Chem. Soc.*, **45**, 96 (1923).

A diagram of the apparatus is shown in Fig. 10. The calorimeter *C* consists of a thin-walled copper vessel in which the substance to be measured is placed. It is wound with silk-covered copper wire which serves both as heater and thermometer. The whole is coated with shellac and covered with gold foil to cut down radiation corrections. The calorimeter is suspended in a massive copper cylinder *B* the inner wall of which is a thin copper cylinder on which is wound a thermometer heater of the same description as that used for the calorimeter. The leads from the calorimeter have a large insulated surface of contact with the cylinder to prevent heat leakage from out side into the calorimeter. The cylinder in turn is suspended from a vacuum-tight container *A*. The whole is placed in a Dewar vessel containing the cooling liquid; for the range 70°–150° K., liquid air is used, 160°–200° K., carbon dioxide-ether mixture and for 200°–270° K., carbon tetrachloride. The great heat capacity of the copper cylinder causes its temperature to remain practically constant even with a difference of 80° between it and the bath.

The following table for glycerol glass illustrates some of the values obtained.

TABLE XX

HEAT CAPACITY OF AMORPHOUS GLYCEROL

Temp. ° K.	C_p per gram atom
70.2	0.734
93.9	0.934
122.0	1.123
153.1	1.336
179.8	1.622
192.6	2.996
227.1	3.205
275.4	3.571
299.4	3.811

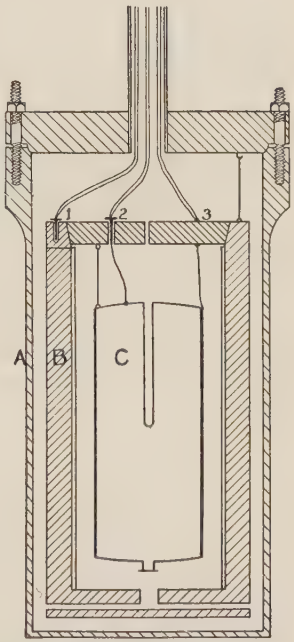

FIG. 10. Vacuum Calorimeter for Specific Heat

Eastman, Williams and Young[1] have collected and critically compared a lot of the data on the specific heat of metals at high temperatures. C_v was found to exceed $3R$ for all metals for which data were available while for typical non-metals this was not the case. For many of the metals there was found to be a correspondence between electropositive characters and increase in heat capacity above 3 *R*. Table XXI gives some of the data collected by these investigators.

[1] *J. Am. Chem. Soc.*, 46, 1184 (1924).

TABLE XXI

Atomic Heats at Constant Pressure

Substance	C_p						
	250° K.	320°	400°	500°	630°	800°	1000°
Sodium	6.44	6.88					
Magnesium	5.95	6.10	6.30	6.57	6.92	7.34	
Aluminum		5.88	6.18	6.48	6.82	7.20	
Calcium		6.22	6.57	7.00	7.50		
Iron		6.05	6.60	7.20	7.90	8.60	
Molybdenum		6.00	6.18	6.38	6.65	7.00	7.45
Platinum	6.15	6.25	6.35	6.47	6.63	6.83	7.10
Lead	6.17	6.35	6.60	6.90			

Zwikker [1] has measured the specific heat of tungsten in the range 90°–2600° absolute. The high temperature measurements were made by two independent methods. The first method depends on the rate of temperature increase of a filament and is determined by the equation

$$I^2R = \text{energy radiated} + C_p \frac{dT}{dt}. \tag{42}$$

The second method depends on the fluctuations of the thermionic emission with the heating current and is given by the equation

$$\theta = \frac{2V\eta}{C_p \cdot d \cdot \nu}, \tag{43}$$

where θ = amplitude of filament temperature fluctuation, V = atomic volume, η = total radiation per cm². of filament surface, d = diameter of filament, ν = frequency of heating current. By use of equation (41) it is possible to calculate the value of C_v. The results obtained are given in Table XXII. C_v appears to be approaching 8 cals. per gram atom at infinite temperatures; above 300° C_p increases linearly with temperature.

Heat of Dissociation: There are a large number of important thermal quantities which cannot be determined by direct thermochemical methods. Many experimental data are however directly related to the heat of reaction and it is thus possible to calculate heats of reaction from a knowledge of equilibrium constants, vapor pressure data, electromotive force measurements, heat losses from hot filaments, absorption spectra and band spectra.

The heat of dissociation of hydrogen has probably been determined in as many diverse ways as any thermochemical quantity. Bichowsky and Copeland [2] have made a direct calorimetric determination of the heat of combination of atomic hydrogen from a Wood's discharge tube. The per-

[1] *Z. Physik*, **52**, 668 (1928).

[2] *J. Am. Chem. Soc.*, **50**, 1315 (1928).

TABLE XXII

SPECIFIC HEAT DATA FOR TUNGSTEN

T/°K	C_p cal/g.atom	$C_p - C_v$ (calc.)	C_v cal/g.atom
100	3.77	0.00	3.77
200	5.32	0.02	5.30
300	5.90	0.03[5]	5.87
600	6.23	0.08[1]	6.15
900	6.57	0.13	6.44
1200	6.90	0.19[1]	6.71
1500	7.23	0.27[2]	6.96
1800	7.56	0.38[2]	7.18
2100	7.89	0.52[7]	7.36
2400	8.22	0.71[7]	7.50
2700	8.56	0.94[1]	7.62
3000	8.89	1.19	7.70

centage dissociation of the hydrogen was determined by the rate of effusion through a small hole. In their experiments the hydrogen diffusing through the hole was 25–30 per cent dissociated. The value obtained for the heat of formation of molecular hydrogen was 105,000 ± 3500 calories. Langmuir [1] has determined the heat of dissociation from a study of the heat losses from a tungsten filament operating in hydrogen.

The loss of heat by conduction and convection from a body at temperature T_2 in a gas at T_1 is

$$W_c = S(\Phi_2 - \Phi_1). \tag{44}$$

S is a shape factor independent of temperature and

$$\Phi = \int_0^T k dT. \tag{45}$$

The effect of dissociation is to increase the heat loss from the body by

$$W_D = SDQ_1c, \tag{46}$$

where D is the diffusion coefficient of hydrogen atoms through molecular hydrogen, Q_1 the heat evolved when 1 gram of hydrogen atoms combine to form molecules and c is the concentration of atomic hydrogen.

H, the heat absorbed by the dissociation of molecular hydrogen at constant pressure was found to be

$$H = 97{,}000 + 3.5T - 0.00045T^2.$$

K. Wohl [2] has obtained the value of 95,000 ± 2000 cals., by use of the explosion method. Bodenstein and Jung [3] calculate a value of 106,700 ± 3000

[1] *J. Am. Chem. Soc.*, **37**, 417 (1915).
[2] *Z. Electrochem.*, **30**, 49 (1924).
[3] *Z. physik. Chem.*, **121**, 127 (1926).

cal. from an analysis of the kinetic data on the thermal and photochemical reaction between hydrogen and bromine. Witmer [1] has made an analysis of a group of lines found in the spectrum of hydrogen in the region 1063–1670 A° when excited in the presence of an excess of argon. Twelve groups of bands are observed corresponding to twelve possible vibrational levels in the normal hydrogen molecule. When the molecule acquires more than twelve vibrational quanta of energy it dissociates. The value obtained for the heat of dissociation in this manner lies between 94,600 and 103,800 with a probable value of 100,100. Condon [2] has obtained a value of 101,400 from a study of the hydrogen molecule on the basis of wave mechanics.

The heat of dissociation of the halogens has been determined thermally from the degree of dissociation on heating and also optically from a study of absorption spectra. These molecules show a complicated system of absorption bands in the red and yellow part of the spectrum converging to a limit from which a continuous absorption extends towards the ultra-violet. The convergence limit represents the longest wave length still capable of dissociating a halogen molecule into a normal and an excited atom.[3] Table XXIII gives a comparison of the values obtained by the two methods.

TABLE XXIII

Heat of Dissociation of Halogens

Halogen	Convergence Limit	$Nh\nu_c$ in kg. cals.	Excitation Energy of Atom kg. cals.	Heat of Dissociation (optical) in kg. cals.	Heat of Dissociation (thermal) in kg. cals.
Cl_2	4785A°	59.4	2.5	56.9	57.0
Br_2	5107	55.6	10.4	45.2	46.2
I_2	4995	56.8	21.6	35.2	34.5

The heat of dissociation of nitrogen, oxygen, nitric oxide and carbon monoxide have been estimated by Birge and Sponer [4] from a study of the band spectra emitted by these molecules. The results for nitrogen have recently been revised [5] in the light of more complete knowledge of the nitrogen spectrum. Kaplan [6] has arrived at a still lower value for nitrogen than that of Birge, while Herzberg [7] has just suggested a lower value for the heat of dissociation of oxygen.

[1] *Proc. Nat. Acad. Sci.*, **12**, 238 (1926)
[2] *Proc. Nat. Acad. Sci.*, **13**, 469 (1927).
[3] Franck, *Trans. Farad. Soc.*, **21**, 536 (1925).
[4] *Phys. Rev.*, **28**, 259 (1926).
[5] Birge and Mulliken, *Nature*, **122**, 842 (1928).
[5] *Phys. Rev.*, **33**, 267 (1929).
[7] *Z. physik Chem.*, (B) **4**, 223, (1929).

Mecke [1] determined the heat of dissociation of oxygen from a study of the predissociation spectrum of NO_2 and from the threshold value of frequency observed in the photochemical decomposition of this molecule. The value obtained is 128,000 cals. and agrees very well with that obtained by Henri [2] from the predissociation spectrum of SO_2. Mecke also calculates values for a number of simple molecular decompositions.

TABLE XXIV

HEATS OF DECOMPOSITION

Reaction	Energy of Decomposition in kg. cals.
$O_2 \rightarrow 2O$	126
$H_2 \rightarrow 2H$	101
$N_2 \rightarrow 2N$	210
$S_2 \rightarrow 2S$	102
$HO \rightarrow H + O$	111
$OH_2 \rightarrow OH + H$	111
$H_2O \rightarrow H_2 + O$	121
$CO \rightarrow C + O$	230
$CO_2 \rightarrow CO + O$	131
$N_2O \rightarrow N_2 + O$	46
$NO_2 \rightarrow NO + O$	77
$\begin{matrix}H\\H\end{matrix}\!>\!C=O \rightarrow H>C=O+H$	90
$CH_4 \rightarrow CH_3 + H$	90
$NH_3 \rightarrow NH_2 + H$	90

THERMOCHEMISTRY OF ORGANIC COMPOUNDS

Heats of Combustion: A great deal of work has been done on heats of combustion since this is practically the only reaction in organic chemistry which takes place smoothly and quickly without any disturbing side reactions, a necessary feature in thermochemical investigation. The combustion takes place in excess of oxygen, and carbon dioxide and water are the usual end products. The heat of combustion is determined at constant volume so that to determine ΔH the quantity ΔnRT must be added to the observed value, Δn being the number of molecules produced less those consumed.

The heat of formation may be calculated from the heat of combustion by subtracting from it the sum of the heats of formation of the carbon dioxide and water resulting from the reaction. For the combustion of sucrose,

$$C_{12}H_{22}O_{11} + 12O_2 = 12CO_2 + 11H_2O; \qquad \Delta H = -1{,}350{,}000 \text{ cals.}$$

The sum of the heats of formation of the carbon dioxide and water gives ΔH

[1] *Z. physik Chem.*, (B), **7**, 108 (1930).

[2] *Nature*, Feb. 22 (1930).

$= -1{,}875{,}300$ cals., so that, for the reaction,

$$12C + 11H_2 + 5\tfrac{1}{2}O_2 = C_{12}H_{22}O_{11}; \qquad \Delta H = -525{,}300 \text{ cals.}$$

The heat of any desired reaction can be calculated directly from the heats of combustion by subtracting the heats of combustion of the substance formed from those for the substances which disappeared. For the reaction

$$C_2H_5OH + C_6H_5COOH = C_6H_5COOC_2H_5 + H_2O,$$

we can calculate from the data in ensuing tables that $\Delta H = +1200$ cals. It is at once seen that this quantity is a difference between two large quantities and is likely to be greatly in error.

Some very important results have been obtained from the heats of combustion of different allotropic modifications of the elements. When the three forms of carbon are burned in oxygen, the heats absorbed are given by the following equations:

$$\begin{aligned} C \text{ (diamond)} + O_2 &= CO_2; & \Delta H &= -94{,}300 \text{ cals.,} \\ C \text{ (graphite)} + O_2 &= CO_2; & \Delta H &= -94{,}800 \text{ " ,} \\ C \text{ (amorphous)} + O_2 &= CO_2; & \Delta H &= -97{,}650 \text{ " .} \end{aligned}$$

It is thus apparent that the internal energy of amorphous carbon is greatest and that for the reaction

$$C \text{ (diamond)} = C \text{ (graphite)}; \qquad \Delta H = +500 \text{ cals.}$$

Similarly, for other allotropic changes, the following heat effects have been observed:

$$\begin{aligned} S \text{ (monoclinic)} &= S \text{ (rhombic)}; & \Delta H &= -230 \text{ cals.,} \\ P \text{ (white)} &= P \text{ (red)}; & \Delta H &= -371 \text{ " ,} \\ O_3 &= 1\tfrac{1}{2}O_2; & \Delta H &= -3620 \text{ " .} \end{aligned}$$

In order that the results of various observers may be compared, it is essential that some standard substance or substances be used, of accurately known heat of combustion, with which to calibrate the calorimeter.

Swientoslawski [1] has discussed all the existing data on calorimetric standards, which include cane sugar, naphthalene and benzoic acid, and concludes that benzoic acid should be used as the absolute standard for all calibration. From a critical study of his own results and those of Dickinson [2] and Fischer and Wrede [3] he gives the following values for the heat of combustion in 15° calories for 1 gram of material weighed in air.

Substance	Heat of Combustion per Gram
Napthalene	9612 cals.
Benzoic acid	6311 "
Cane sugar	3945 "

[1] *J. Am. Chem. Soc.*, **39**, 2595 (1917).

[2] Bur. Standards, Sci. Paper **230**.

[3] *Sitzb. k. akad. Wiss. Math. Nat. Klasse*, 1908, 129.

Salicylic acid has also been proposed [1] as a standard substance and its method of preparation discussed. The value given is 5242 g. cals. (15° cals.) per gram of substance weighed in air.

The Third International Union of Pure and Applied Chemistry (Lyons, 1922) adopted benzoic acid as a primary standard for calibration purposes and gave the value of 6324 g. cals.

Heats of Atomic Linkage: Fajans [2] has developed a method for calculating the heat of formation from atomic carbon and hydrogen. The heats of formation of organic compounds, as given in the literature, are always related to solid carbon and molecular hydrogen. These results are not suited for theoretical treatment since they are mostly small numbers expressing the algebraic sum of larger quantities. It is now possible to calculate the energy involved in the various linkages in the compound.

TABLE XXV

ΔH FOR HYDROCARBONS IN K. CALS.

Substance	ΔH	Increase in ΔH for CH_2
Methane	−210.8	
		157.6
Ethane	−368.4	
		157.9
Propane	−526.3	
		157.1
Isobutane	−683.4	
		154.9
n-pentane	−838.3	
		160.7
n-hexane	−999.0	
		158.5
n-heptane	−1,157.5	
		155.6
n-octane	−1,313.1	
		153.1
Decane	−1,619.2	
Benzene	−783	
		153
Toluene	−936	
		155
Ethyl benzene	−1,091	
		158
Isopropyl benzene	−1,247	
		153
Tert. butyl benzene	−1,400	
		154
Penta methyl benzene	−1,554	
		158
Hexa methyl benzene	−1,712	

[1] Cohen, Verkade, Miyake, Coops and Howe, *Z. physik. Chem.*, **126**, 290 (1927).
[2] *Ber.*, **53**, 643 (1920); **55**, 2836 (1922); *Z. physik. Chem.*, **99**, 395 (1921).

From the X-ray experiments of the Braggs we know that, in the diamond, each C-atom is in the middle of a regular tetrahedron at whose corners are four other C-atoms which are located in exactly the same manner with respect to other C-atoms. In saturated aliphatic compounds the C-atoms are tetravalent and the forces existing are very closely connected with those found in the diamond. The energy of linkage between two carbon atoms in the diamond is very nearly the same as that between two carbon atoms in a saturated aliphatic compound.

TABLE XXVI

INCREASE IN HEAT OF COMBUSTION DUE TO CH_2

Substance	ΔH	Increase in ΔH
Formic	−62.8	
		145
Acetic	−208	
		157
Propionic	−365	
		155
n-butyric	−520	
		159
n-valeric	−679	
		152
Caproic	−831	
		155
Heptylic	−986	
		160
Dipropyl acetic	−1,146	
		141
Heptyl acetic	−1,287	
		166
Capric	−1,453	
		157
Undecylic	−1,610	
		162
Lauric	−1,772	
		157
Myristic	−2,086	
		147
Palmitic	−2,380	
		159
Stearic	−2,698	
		156
Arachidic	−3,010	
		164
Behenic	−3,338	
Average		155.7

The values obtained in combustion experiments may be considered as made up of several simpler quantities: x, the heat of formation of the C–H linkage; y, the heat of formation of C–C linkage; v, the heat of formation of liquid water from 1 g-atom of atomic hydrogen and molecular oxygen and z, the

heat of formation of gaseous carbon dioxide from 1 g. atom of atomic carbon and molecular oxygen. For propane and ethane

$$-8x + 8v - 2y + 3z = -526{,}700 \quad (47)$$

$$-6x + 6v - y + 2z = -370{,}900 \quad (48)$$

$$-2x + 2v - y + z = -155{,}800 \quad (49)$$

The result is the increase in the heat of combustion of a molecule for an increase of a CH_2 group. This increase of CH_2 always gives approximately the same change in the heat of combustion as is illustrated by Table XXV.

This means that the magnitude $y + 2x$ is only subject to minor variations; the simplest assumption to explain this is that both y and x are constant; the energies of the C–C and the C–H linkages in different saturated aliphatic compounds are approximately the same. Still further support for the constancy of these quantities is found in the work of Richards and Davis [1]; they have measured the heat of combustion of a number of compounds with a high degree of precision. Table XXVI gives further support for the constancy in the increase of the heat of combustion as one proceeds through an homologous series.

Further evidence goes to show that the energy of a C–C linkage in hydrocarbons is constant and does not depend on whether the other linkages of the carbon atom are with hydrogen or other carbon atoms. This point is well illustrated by the work of Richards and Jesse [2] on the isomeric octanes.

TABLE XXVII

Heats of Combustion of Isomeric Octanes in K. cals.

Substance	Heat of Vaporization	ΔH (Liquid)	ΔH (Vapor)
n-octane	−8.120	−1,300.5	−1,308.6
2 methyl heptane	−7.880	−1,301.9	−1,309.8
2.5 dimethyl hexane	−7.650	−1,299.2	−1,306.9
3.4 " "	−7.880	−1,299.7	−1,307.6
3 ethyl hexane	−7.880	−1,298.3	−1,306.2
		Mean	−1,307.8

If one eliminates x and v from equations (47) and (48) one obtains the relationship

$$z - 2y = -96{,}500 \text{ cals.} \quad (50)$$

A mean value of $z - 2y$ has been obtained from the results given in Tables XXVI and XXVII.

[1] *J. Am. Chem. Soc.*, **42**, 1599 (1920).
[2] *J. Am. Chem. Soc.*, **32**, 292 (1910).

The constancy of the value obtained, $-98{,}000 \pm 8{,}000$ calories, is not good and the variations are mostly due to experimental error. This value is comparable with the heat of combustion of the diamond, $\Delta H = -94{,}000$ cals.

To proceed further, it is necessary to evaluate y the energy of the C–C linkage and this is the most uncertain value in these calculations. At present it has not lent itself to direct calorimetric determination and has been calculated indirectly from the effect of pressure on the temperature of the positive crater in the carbon arc. A number of investigators[1] have attempted to determine the heat of evaporation of carbon. The assumption underlying these investigations is that equilibrium conditions exist in the carbon arc, the positive crater coming to such a temperature that the vapor pressure of carbon

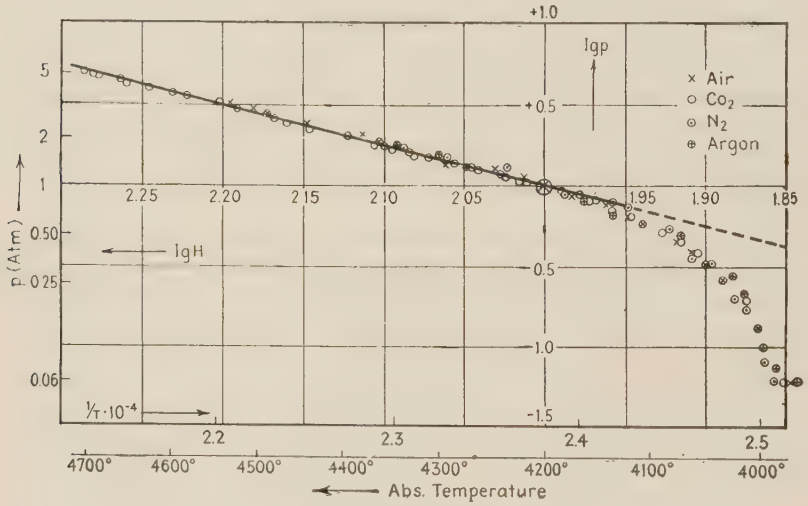

Fig. 11. Vapor Pressure Curve of Carbon

is the same as that of the inert gas present. After a "normal load" for the arc is reached at any optional pressure the temperature reaches a maximum value and then remains constant for a very large increase in load. The maximum temperature for any given pressure is independent of the nature of the gas present (CO_2, air, Ar, N_2). All the results obtained show that the equilibrium temperature of the crater is independent of the electrical conditions or of the chemical reactions taking place in the arc. The vapor pressure curve is given in Fig. 11; in the pressure interval 0.8 to 5 atmospheres the linear relationship required by the Clausius-Clapeyron equation is obtained. The deviations observed at lower temperatures may be due to changes in the light absorption of graphite or to superheating phenomena. The value for the heat

[1] Kohn and Guckel, *Naturwiss.*, **12**, 139 (1924); *Z. Physik*, **27**, 305 (1924); Wertenstein and Jedrzejewski, *Compt. rend.*, **177**, 316 (1923); Ryschkewitsch, *Z. Electrochem.*, **31**, 54 (1925); Fajans, *ibid.*, **31**, 63 (1925).

of vaporization obtained from this curve is

$$\Delta H_{300^\circ} = -139{,}200 \text{ cals.}$$

as compared with a value of − 141,400 calculated with the aid of a theoretical chemical constant. Rschkewitsch and Fajans place the melting point of carbon at about 3800° with an equilibrium pressure of $\frac{1}{3}$ atmosphere. The latent heat of fusion is very roughly calculated to be − 10,000 cals. When these values are reduced to room temperature a value of − 147,000 cals. is obtained for the heat of sublimation of carbon. This value is equal to $-2y$ the energy of two C–C linkages and gives a value

$$z = -245{,}000 \text{ cals.}$$

for the heat of combustion of monatomic carbon vapor. The heat of combustion v of atomic hydrogen is − 84,200 ± 3,000 cals. which leads to a value for x the energy of a C–H linkage of − 92,400 cals.

In the customary tables for heats of formation of organic compounds from diamond and molecular hydrogen ΔH usually has a small value numerically and is positive in the case of some unsaturated compounds. When we calculate the heat of formation from the atoms the value is always a large negative quantity as is illustrated in Table XXVIII.

TABLE XXVIII

Heat of Formation of Aliphatic Compounds from Atoms in k. cals.

Substance	Heat of Combustion	Heat of Formation from Diamond $+H_2$	Heat of Formation from Atoms	ΔH for CH_2
Methane	−210.8	−19.8	−368.8	
				−252.9
Ethane	−368.4	−24.7	−621.7	
				−252.6
Propane	−526.3	29.3	−874.3	
Ethylene	−332.	7.0	−492	
				−249
Propylene	−490.2	2.7	−741	

From the work of Debye and Scheerer on the structure of graphite we know that the carbon atoms lie in parallel planes and that the atoms in any plane are arranged in regular hexagons similar to the carbon atoms in a benzene nucleus. The various planes are held very loosely together, a fact easily visible in the cleavage of graphite; the fourth linkage of a C-atom in graphite is much weaker than the other three. Steiger [1] has calculated the energies of

[1] *Ber.*, **53**, 666 (1920).

the C–C and C–H linkage in aromatic hydrocarbons on the assumption that one of the carbon bonds can be neglected in comparison to the other three. From these considerations one arrives at a value for the energy of C–C in aromatic compounds as $\Delta H = -96{,}700$ and for the C–H linkage $\Delta H = -102{,}200$. Table XXIX gives a synopsis of the various values obtained for the energies of the various linkages.

TABLE XXIX

Energy of Linkage in Carbon Compounds

Linkage	ΔH from atoms	
C–C	−73,500	aliphatic
C–H	−92,400	aliphatic
C=C	−122,900	aliphatic
C≡C	−161,600	aliphatic
C–C	− 96,700	aromatic
C–H	−102,200	aromatic

Table XXX gives the heat of combustion of a number of saturated compounds C_nH_{2n+2} and the corresponding compounds containing one double bond $C_{n+1}H_{2n+2}$. If the difference between the heats of combustion of these compounds is subtracted from the heat of combustion of atomic carbon the energy of the C = C linkage is obtained.

TABLE XXX

Heats of Combustion of Various Organic Compounds in k. cals.

Compound	Formula	ΔH	Difference
Methane	CH_4	−210.8	−121.2
Ethylene	C_2H_4	−332	
Methyl chloride	CH_3Cl	−164.7	−121.5
Mono chlor ethylene	C_2H_3Cl	−286.2	
Trimethyl methane	C_4H_{10}	−683.4	−120.
Amylene	C_5H_{10}	−803.4	−124.7
Diallyl	C_5H_{10}	−928.1	

These values are due to Thomsen and lead to a value for C = C of − 122,900 calories.

Considering the two oxides of carbon as formed from atomic carbon and oxygen

$$C_{(\text{vapor})} + \tfrac{1}{2}O_2 = CO; \qquad \Delta H = -174{,}000;$$

$$CO + \tfrac{1}{2}O_2 = CO_2; \qquad \Delta H = -67{,}000;$$

The energy accompanying the addition of the first oxygen atom is much greater than with the second.

Thermochemistry of Inorganic Compounds

Berkenheim [1] has pointed out that the heat of formation of any binary inorganic compound is approximately the arithmetic mean of the heats of formation of equivalent weights of the corresponding compounds of the elements which are adjacent to the one considered in the periodic table. It is thus possible to determine unknown heats of formation and point out the possibility of error in known values.

TABLE XXXI

Heat of Formation of Inorganic Compounds

NaCl	$\frac{MgCl_2}{2}$	$\frac{AlCl_3}{3}$	$\frac{SiCl_4}{4}$	$\frac{PCl_5}{5}$
97.9	75.5 (calc. 75.8)	53.61 (calc. 54.4)	33.34 (calc. 37.3)	21.0
	$\frac{MgO}{2}$	$\frac{Al_2O_3}{6}$	$\frac{SiO_2}{4}$	$\frac{P_2O_5}{10}$
	71.95	63.3 (calc. 60.3)	48.7 (calc. 50.1)	36.94
$\frac{MgCl_2}{2}$	$\frac{CaCl_2}{2}$	$\frac{SrCl_2}{2}$	$\frac{BaCl_2}{2}$	
75.6	84.9 (calc. 84.0)	92.3 (calc. 91.7)	98.5	

Curves of the type shown in Fig. 12 can be obtained for the heat of formation as a function of the ordinal number of the element. Irregular values on such a curve would justify a re-investigation of the heat of formation in question. It also helps to decide between the work of various investigators whose values differ widely.

Lattice Energies: In recent years the thermochemistry of polar, salt-like compounds has received a considerable impulse from the work of Born [2] on the *lattice energy* of crystals, which is defined as the energy necessary to form free gas ions from a crystal. The energy of the crystal lattice is formulated in terms of the electrostatic attraction of the ions and repulsive forces between the atoms due to the electrons concentrated about each nucleus. This leads to an equation for the lattice energy.

$$U = \frac{Na}{4\partial}\left(\frac{n-1}{n}\right). \qquad (51)$$

[1] *Z. physikal. Chem.*, **136**, 231 (1928).
[2] *Ber. deut. physik. Ges.*, **21**, 13 (1919).

N is the Avogadro constant, ∂ the lattice constant for the crystal, a is the constant for the attractive force and n the exponent of the distance for the repulsive force.

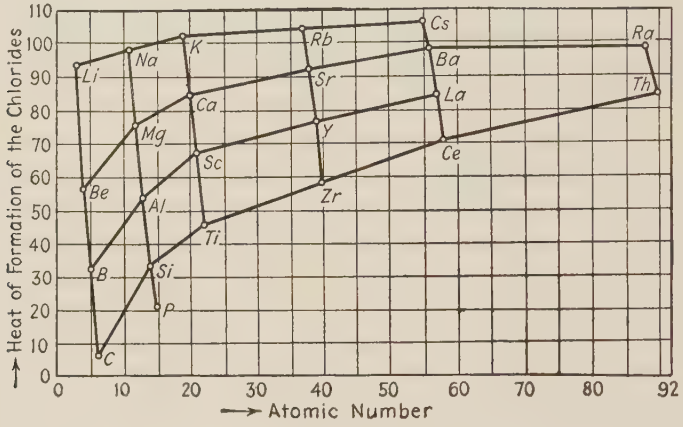

Fig. 12. Heats of Formation of Inorganic Chlorides

It is possible to calculate the lattice energy by a cyclical process from measurable thermal quantities.

$$\begin{array}{ccc} [M],\ \tfrac{1}{2}X_2 & \xrightarrow{Q_{MX}} & [MX] \\ \uparrow S_M \mid D_X & & \downarrow -U_{MX} \\ M,\ X & \xleftarrow[-E_X]{I_M} & M^+,\ X^- \end{array}$$

A mol. of solid metal M unites with half a mol. of halogen X_2 to form solid MX with an evolution of Q_{MX} calories. This solid is broken down to gas ions, M^+, X^- with the absorption of the lattice energy U_{MX} calories. These become neutral atoms with the liberation of the ionization energy of the metal atom I_M and the absorption of the electron affinity energy of the halogen E_X. The metal atoms now condense to solid with the liberation of the heat of sublimation S_M and the halogen atoms combine with the liberation of the heat of dissociation D_X. This returns us to the initial state so that by Hess' Law

$$Q_{MX} - U_{MX} + (I_M + S_M) + (D_X - E_X) = 0. \qquad (52)$$

Table XXXII gives the results of this calculation for the strontium halides.

TABLE XXXII

CALCULATION OF U BY BORN'S CYCLICAL PROCESS

	Q_{SrCl_2}	Q_{SrBr_2}	Q_{SrI_2}
S_{Sr}—heat of sublimation	32.5	32.5	32.5
I_{Sr}—heat of ionization	380.0	380.0	380.0
$2D_{X_2}$—heat of dissociation	59.5	46.2	34.5
Q—heat of formation	184.7	170.2	150.0
	656.7	628.9	597.0
$2E_{X_2}$—heat of charging	178.6	174.0	163.6
U—lattice energy	478.1	454.9	433.4
U (calc.)	476.0	455.0	434.0

Berkenheim [1] has pointed out that the same regularities hold for all the quantities involved in this calculation that he found in the heats of formation of inorganic compounds. The heat of dissociation of bromine is 46.2 k.cals. as compared to a mean value for chlorine and iodine of 45.7. The same relationships hold amongst the heats of sublimation of the alkali metals. A similar relationship is found to hold amongst the ionizing energies of atoms. The ionizing energy used, however, is the arithmetic mean of the energies necessary to remove all the electrons from the outer shell. The values used for making this comparison are taken from a table given by Dushman.[2]

TABLE XXXIII

ENERGIES TO REMOVE OUTER SHELL ELECTRONS

Element	Total Energy	Average Energy	Mean Energy (calc.)
Li	125.0	125.0	
Be	637.3	318.6	333.8 k. cals.
B	1628	542.6	577
C	3349	837	887
N	6164	1233	1239
O	9850	1642	1663
F	14628	2093	
Na	118.7	118.7	
Mg	521.7	260.8	260.8
Al	1209	403	427.9
Si	2380	595	606
P	4052	810	812
S	6170	1028	1056
Cl	9084	1298	

[1] *Loc. cit.*

[2] *Chem. Rev.*, 5, 159 (1928)

The energy involved in the electrostatic attraction between a positively charged ion and the negatively charged ions Cl′, Br′, I′, O″ and S″ will now be considered. It is found that, in all these cases, the lattice energy is the arithmetic mean of the energies for adjacent elements in the periodic table whether the variables be the positive or the negative ions.

TABLE XXXIV

Lattice Energies for Halogen Compounds

	Chlorides	Bromides	Iodides	Bromides (calc.)
Li	205	191	176	190.5
Na	181	169	156	168.5
K	165	154	143	154.0
Rb	160	150	139	149.5
Cs	154	145	135	144.5
Mg	597	567	540	568.5
Ca	513	484	459	486.0
Sr	489	462	436	462.5
Ba	452	430	403	427.5

Thermochemistry of Solutions

Heat of Solution: By *heat of solution* one understands the amount of heat that is absorbed when one mol. of a substance is dissolved in so large a volume of solvent that further dilution causes no further absorption of heat. The heat absorbed when 1 mol. of a substance is dissolved in a solvent to form a given solution is called the *total heat of solution.* If, however, a small amount of solute is added to a given solution, the heat evolved per mol. is called the *partial heat of solution* for that particular concentration. These two quantities are identical in very dilute solutions, but, for concentrated solutions, they may be very different from one another.

Gehloff [1] has shown that the heat of solution of a number of substances such as hydrocarbons and aromatic amines in a wide variety of solvents is approximately constant and equal to or greater than the latent heat of fusion of the substance. One can explain this by assuming that the main part of the heat of solution consists of the energy necessary to overcome the energy of the crystal lattice and break it down into simple molecules. Substances containing OH-groups in particular and also nitro compounds which are associated in solution have a heat of solution which is much smaller than the heat of fusion. In the case of substances having a " normal " heat of solution the temperature coefficient of solubility must be the same in all solvents and directly calculable from the heat of fusion. Table XXXV shows the nature of the agreement obtained.

[1] *Z. physik. Chem.*, **98**, 255 (1921).

TABLE XXXV

HEATS OF SOLUTION IN CALS. PER GRAM

Substance	Water	Benzol	Ether	Alcohol	Carbon Disulfide	Acetone	Amyl Acetate	Average Heat of Solution	Heat of Fusion
Napthalene	——	34.5	37.9	36.5	39.1	34.1	——	35.9	35.7
Diphenyl	——	28.3	——	27.6	——	29.0	——	28.3	28.5
Diphenylamine	——	24.0	20.7	——	21.2	19.1	21.0	21.2	21.3
Azobenzol	——	27.8	27.1	28.8	27.3	30.3	27.1	28.1	29.2
Nitronaphthalene	——	31.1	33.4	——	31.3	(40.3?)	25.9	28.3	25.3
Phenol	26.7	45.0	3.78	5.5	——	1.5	——		24.9
Pyrogallol	4.8	——	3.3	−6.8	——	−11.0	0		——
Chloralhydrate	4.7	——	0	5.8	——	3.8			33.0

Table XXXVI illustrates the wide divergence observed in heats of solution.

TABLE XXXVI

INTEGRAL HEATS OF SOLUTION FOR METALLIC COMPOUNDS

Substance	Mols. H_2O per Mol. Salt	ΔH
LiOH	400	−5,800
NaOH	200	−9,900
KOH	250	−13,300
$BaCl_2$	400	2,100
$BaCl_2 2H_2O$	400	4,900
$FeCl_2$	350	−17,900
$FeCl_2 4H_2O$	400	−2,750
$CaBr_2$	400	−24,510
$CaBr_2 6H_2O$	400	1,100
$ZnSO_4$	400	−18,400
$ZnSO_4 7H_2O$	400	4,260
$Ca(NO_3)_2$	400	−3,950
$Ca(NO_3)_2 4H_2O$	400	7,250
$CaSO_4$	∞	−4,400
$CaSO_4 2H_2O$	∞	300
CaI_2	400	−27,700

Comparing the heats of solution with one another, it is seen that anhydrous salts which can be in equilibrium with their saturated solutions at room temperature usually dissolve with an absorption of heat while anhydrous salts which form hydrates at room temperature generally dissolve with evolution of heat since their heats of hydration are generally very large.

Heat of Hydration of Gas Ions: Fajans[1] has introduced a new magnitude called the *heat of hydration of gas ions* which plays an important role in the theory of solutions. The heat of solution of a salt is the difference between the heat necessary to dissociate the crystal into free gas ions; i.e., the lattice energy, and the heat of solution of these same ions in water.

$$L = U - W^+ - W^-, \tag{53}$$

where L is the heat of solution, U the lattice energy and W^+, W^- the heat of hydration of the gas ions. From this equation it can be seen that L is the difference between two very large quantities. The actually observed values for L vary over a wide range and have both positive and negative values.

Fajans has calculated the heat of hydration of gas ions making use of lattice energy data and also by an alternative method which will be discussed shortly.

$$\begin{aligned} K^+(g) + Cl^-(g) &= KCl(s) + U \\ KCl(s) + aq &= K^+ aq + Cl^- aq + L \\ \hline K^+(g) + Cl^-(g) + aq &= K^+ aq + Cl^- aq + (U + L) \end{aligned}$$

[1] *Ber. deut. physik. Ges.*, **21**, 549, 714 (1919).

where U is obtained from lattice energy data, L is the heat of solution and $(U + L) = W$, where W is the heat of hydration of the gas ions. Fajans gives the following table of values for W for a number of alkali halides.

TABLE XXXVII

Salt	W_{salt}	Salt	W_{salt}	Salt	W_{salt}
LiCl	− 187,000	LiBr	− 178,000	LiI	− 168,000
NaCl	− 180,500	NaBr	− 171,000	NaI	− 159,000
KCl	− 159,000	KBr	− 150,000	KI	− 139,000
RbCl	− 150,000				
CsCl	− 151,000				
TlCl	− 159,000				

The values of W for the salts are purely additive quantities, depending on the values for the individual gas ions, so that, if differences are taken for a series of salts for two metals with common cations, the same values should be obtained. Table XXXVIII illustrates this.

TABLE XXXVIII

	Cl	Br	I
$W_{Li^+} - W_{K^+}$	− 28,000	− 28,000	− 29,000
$W_{Na^+} - W_{K^+}$	− 21,500	− 21,000	− 20,000

Fajans[1] has developed another method for determining the differences between the heats of hydration of two gas ions independent of the lattice energy concept. The method employed is illustrated by the following process:

$K(s) + aq = K^+aq + OH^-aq + \frac{1}{2}H_2(g)$;	$\Delta H = -48{,}100$,	(a)
$H^+aq + OH^-aq = aq$;	$\Delta H = -13{,}600$,	(b)
$K(s) + H^+aq = \frac{1}{2}H_2(g) + K^+aq$;	$\Delta H = -61{,}700$,	(c)
$K(g) = K(s)$;	$\Delta H = -21{,}000$,	(d)
$K^+(g) + \ominus = K(g)$;	$\Delta H = -99{,}000$,	(e)
$\frac{1}{2}H_2(g) = H(g)$;	$\Delta H = +45{,}000$,	(f)
$H(g) = H^+(g) + \ominus$;	$\Delta H = 312{,}000$,	(g)

whence

$K^+(g) + H^+aq = H^+(g) + K^+aq$;	$\Delta H = 175{,}000$,	(h)

and since

$H^+(g) + aq = H^+aq$;	$\Delta H = W_{H^+}$,	(i)
$K^+(g) + aq = K^+aq$;	$\Delta H = W_{K^+}$,	(j)

[1] *Ber. deut. physik. Ges.*, **20**, 712 (1919).

equation (h) gives us

$$W_{H^+} - W_{K^+} = -175{,}000 \text{ cals.}$$

Equations (a) and (b) give the heat effect of two reactions that take place in solutions, (d) gives the heat of sublimation of potassium, (f) the heat of dissociation of hydrogen, (e) the heat effect corresponding to the ionization potential of potassium and (g) that corresponding to the ionization potential of atomic hydrogen. Other reactions have been worked out in an analogous manner and the following values obtained:

$$W_{Na^+} - W_{K^+} = -16{,}000 \pm 4000 \text{ cals.},$$
$$W_{K^+} - W_{Rb^+} = -6000 \pm 4000 \text{ cals.}$$

These values agree fairly well with those calculated from the lattice energy data.

Born [1] has calculated the heat of hydration of individual gas ions on the assumption that the total hydration effect is of electrostatic origin. The ions are considered as spheres and the heat of hydration is assumed equal to the energy obtained from discharging the spheres in vacuum and charging them subsequently in water, the work of solvation being given by the formula

$$A = \frac{e^2 z^2}{2r}\left(1 - \frac{1}{D}\right), \tag{54}$$

where r is the radius of the ion and D the dielectric constant of the medium. Webb [2] has pointed out that the energy change obtained by this calculation is a free energy change and not the total energy as has been assumed previously in the literature. He has made a more precise calculation of the energy of hydration taking into account the non-homogeneity of the medium and the energy required to compress the solvent in the neighborhood of the ion

It is also possible to calculate heats of hydration of individual ions from a knowledge of absolute electrode potentials by means of the equation

$$U = -S - I + n\xi_{Hg} + W^+. \tag{55}$$

U is the total energy of a given elementary electrode process taking the value of zero for the dropping mercury electrode, S is the heat of sublimation of the element in question, I the heat of ionization, ξ_{Hg} is of opposite sign to the energy necessary to evaporate electrons from mercury and has a value of 104 k. cals., and W^+ is the heat of hydration of the gas ion. In Table XXXIX the values obtained by this method and those calculated by Born and Webb are listed.

When we possess accurate data for lattice energies and heats of hydration of gas ions we can calculate the solubility of an electrolyte in any solvent. It is the difference between the lattice energy and the free energy of solvation which determines the solubility of an electrolyte.

[1] *Z. Physik*, **1**, 4 (1920).

[2] *Proc. Nat. Acad. Sci.*, **12**, 524 (1926); *J. Am. Chem. Soc.*, **48**, 2589 (1926).

TABLE XXXIX

HEATS OF HYDRATION OF GAS IONS

Ion	From single potential	Calc. (Born)	Calc. (Webb)
H^+	268	262	249.6
Li^+	150	110	——
Na^+	117	103	99.0
K^+	97	82	81.9
Rb^+	92	73	76.9
Cs^+	86	74	71.5
F^-	102	——	87.0
Cl^-	63	77	70.1
Br^-	52	68	66.2
I^-	41	57	61.0
Ag^+	125	——	95.5
Tl^+	——	——	78.6
Zn^{++}	——	——	525
Cd^{++}	——	——	473
Hg^{++}	——	——	486
S^{--}	——	——	54

Partial Heats of Solution: In thermodynamic calculations the partial heats of solution are the quantities employed and the accompanying illustration will show how these quantities may be derived from the total heats of solution which are the quantities usually found in the literature.

Brönsted [1] has measured the heats of formation of sulphuric acid solutions from H_2SO_4 and H_2O and his values are given in Table XL.

The third column gives the heat absorbed per mol. of solution formed. In Fig. 13 the heat of formation per mol. of solution from acid and water is plotted as ordinate against the mol. fraction of acid as abscissa. A tangent to the curve is drawn at $N_2 = 0.50$; the intercepts of this tangent on the ordinates $N_1 = 1$ and $N_2 = 1$ are equal respectively to $\overline{H}_1$ and $\overline{H}_2$, where

$$\overline{H}_1 = \frac{\partial H}{\partial n_1} \quad \text{and} \quad \overline{H}_2 = \frac{\partial H}{\partial n_2},$$

where n_1 and n_2 are the number of mols. of water and acid in any given amount of solution. To prove this relationship,

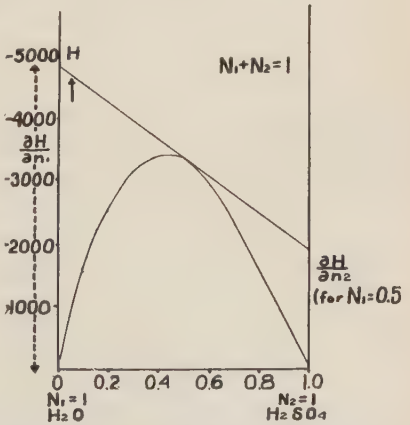

FIG. 13. Heat of Solution of H_2SO_4

[1] *Z. physik. Chem.*, 68, 700 (1909).

TABLE XL

HEATS OF SOLUTION OF SULPHURIC ACID AND WATER

Mol. Fraction Acid—N_2	Heat Evolved per Mol. Acid	ΔH per Mol. Soln.	Mol. Fraction Acid—N_2	Heat Evolved per Mol. Acid	ΔH per Mol. Soln.
0.00008	20,430	− 1.6	0.10	15,610	− 1561
0.00016	20,150	− 3.2	0.15	14,170	− 2125
0.00024	19,900	− 4.78	0.20	12,940	− 2588
0.00032	19,660	− 6.14	0.25	11,880	− 2969
0.00040	19,400	− 7.76	0.30	0,710	− 3213
0.000625	18,990	− 11.87	0.35	9,650	− 3378
0.00125	18,540	− 23.2	0.40	8,630	− 3452
0.00250	18,100	− 45.2	0.45	7,680	− 3456
0.0050	17,760	− 88.8	0.50	6,730	− 3365
0.01	17,600	− 176	0.55	5,810	− 3195
0.02	17,360	− 347.2	0.60	4,870	− 2932
0.03	17,200	− 516	0.65	4,060	− 2639
0.04	17,060	− 682.4	0.70	3,280	− 2296
0.05	16,900	− 845	0.75	2,600	− 1950
0.06	16,710	− 1002.6	0.80	1,970	− 1576
0.07	16,460	− 1152.2	0.85	1,420	− 1207
0.08	16,200	− 1296	0.90	930	− 837
0.09	15,910	− 1431.9	0.95	450	− 427

it is necessary to show that

$$H - N_2\frac{dH}{dN_2} = \frac{\partial H}{\partial n_1}, \tag{56}$$

where the mol. fraction of acid N_2 is equal to $\frac{n_2}{n_1 + n_2}$. Since

$$H = \frac{\boldsymbol{H}}{n_1 + n_2}, \tag{57}$$

where $\boldsymbol{H}$ is the heat content of a solution containing n_1 mols. of water and n_2 mols. of acid,

$$dH = \frac{d\boldsymbol{H}}{n_1 + n_2} - \frac{dn_1}{(n_1 + n_2)^2} \tag{58}$$

and $dN_2 = -\frac{n_2 dn_1}{(n_1 + n_2)^2}$, if we assume n_2 constant and vary N_2 by varying n_1. Then

$$N_2\frac{dH}{dN_2} = -\frac{dH}{dn_1} + \frac{H}{n_1 + n_2} = -\frac{\partial H}{\partial n_1} + H. \tag{59}$$

Substituting this in the original equation the result follows. It can also be shown that

$$\boldsymbol{H} = n_1\frac{\partial H}{\partial n_1} + n_2\frac{\partial H}{\partial n_2} \tag{60}$$

and

$$\frac{dH}{dN_1} = -\frac{dH}{dN_2} = \frac{\partial H}{\partial n_1} - \frac{\partial H}{\partial n_2}. \tag{61}$$

The quantity $\frac{\partial H}{\partial n_1}$ is the partial heat of solution of water in the acid solution of mol. fraction N_2 or the partial molal heat content of the water in the solution. Hence the intercept of the tangent on the ordinate $N_2 = 1$ gives the partial heat of solution of 1 mol. of acid in a large quantity of solution of mol. fraction $N_2 = 0.50$.

In a very similar manner the heat effect when one mol. of solution of composition $N_2 = 0.20$ is added to a large quantity of composition $N_2 = 0.50$ can be determined. The intercept of the ordinate at $N_2 = 0.20$ between the curve and the tangent to the curve at $N_2 = 0.50$ gives the measure of this heat effect. This can be shown as follows:

0.2 mol. acid + l.q. soln. ($N_2 = 0.50$);	$\Delta H = 0.2\bar{H}_2$ ($N_2 = 0.50$),
0.8 mol. water + l.q. soln. ($N_2 = 0.50$);	$\Delta H = 0.8\bar{H}_1$ ($N_2 = 0.50$),
0.2 mol. acid + 0.8 mol. water;	$\Delta H = H$ ($N_2 = 0.20$),
1 mol. soln. ($N_2 = 0.20$) + l.q. soln. ($N_2 = 0.50$);	$\Delta H = ?$,
$? = 0.2\bar{H}_2$ ($N_2 = 0.50$) + $0.8\bar{H}_1$ ($N_2 = 0.50$) − H ($N_2 = 0.20$).	

This corresponds to the intercept mentioned above. In general when 1 mol. of solution of composition x_1 is mixed with a large quantity of solution of composition x_2, the heat effect is calculated by drawing a tangent to the curve at x_2 and determining the distance from where this cuts the ordinate x_1 to the curve.

If one mol. of solution of composition $N_2 = 0.20$ is mixed with three mols. of composition $N_2 = 0.60$, the heat effect can be determined in a similar manner.

0.2 mol. acid + 0.8 mol. water;	$\Delta H = H$ ($N_2 = 0.20$),
3 × 0.6 mol. acid + 3 × 0.4 mol. water;	$\Delta H = 3H$ ($N_2 = 0.60$),
2 mol. acid + 2 mol. water;	$\Delta H = 4H$ ($N_2 = 0.50$),
1 mol. soln. ($N_2 = 0.20$) + 3 mol. soln.;	($N_2 = 0.60$) $\Delta H = ?$,
$? = 4H$ ($N_2 = 0.50$) − H ($N_2 = 0.20$) − $3H$ ($N_2 = 0.60$).	

In the diagram the chord joining the points on the curve corresponding to $N_2 = 0.50$ and $N_2 = 0.60$ is produced to cut the ordinate at $N_2 = 0.20$ and the distance between this point and the curve gives the heat effect.

Relative Nature of Values for Heat Content Used: H is the molal heat content of the solution when the molal heat contents of the pure acid and water are assumed to be zero and similarly $\bar{H}_1$ and $\bar{H}_2$ are the partial molal heat contents of the water and acid in the solution referred to the heat content of the pure substances as zero.

Of course it is not necessary to make these particular assumptions concerning the position of the zero point on the diagram. We might have considered the heat content of the system $SO_3 + H_2O$ as zero when $N_2 = 1$, in which case the zero or base line of the curve would be displaced to 20,400 on the ordinate $N_2 = 1$ on the present diagram. The base line might even have been considered as drawn between the points giving the heat contents of the elements from which the water and acid are formed. Lewis and Randall[1] use as their base line the heat contents of the substances in infinitely dilute

[1] Thermodynamics. McGraw-Hill Co., page 88.

solutions. Fig. 14 shows the positions of these various base lines with reference to the curve. It will be seen from the above discussion that the absolute values assigned to the various points is of no importance since we are dealing solely with ΔH which is the difference between two H's. The particular values assigned to the various points have no physical significance since we are unable to determine absolute values for the heat content of any substance.

Calculation of Partial Molal Heat Content for the Solvent when that for Solute is Known: We know that

$$H = n_1 \frac{\partial H}{\partial n_1} + n_2 \frac{\partial H}{\partial n_2}$$

and, since

$$dH = \frac{\partial H}{\partial n_1} dn_1 + \frac{\partial H}{\partial n_2} dn_2, \qquad (62)$$

it can be seen that

$$n_1 d\left(\frac{\partial H}{\partial n_1}\right) + n_2 d\left(\frac{\partial H}{\partial n_2}\right) = 0. \qquad (63)$$

So

$$\int d\left(\frac{\partial H}{\partial n_1}\right) = -\int \frac{N_2}{N_1} d\left(\frac{\partial H}{\partial n_2}\right). \qquad (64)$$

If, now, the values of $\frac{\partial H}{\partial n_2}$ are given, it is possible to determine those for $\frac{\partial H}{\partial n_1}$ if the value is known for $\frac{\partial H}{\partial n_1}$ when $\frac{\partial H}{\partial n_2} = 0$. To do this, the values of $\frac{N_2}{N_1}$ are plotted as ordinates against $\frac{\partial H}{\partial n_2}$ as abscissæ. The negative value of the area under the curve between $N_1 = 0$ and $N_1 = N_1'$ gives the difference between the values of $\frac{\partial H}{\partial n_1}$ for $N_1 = N_1'$ and $N_1 = 0$. To determine a series of values of $\frac{\partial H}{\partial n_1}$, it is necessary to know from experiment the limiting value of $\frac{\partial H}{\partial n_1}$ as N_1 approaches zero.

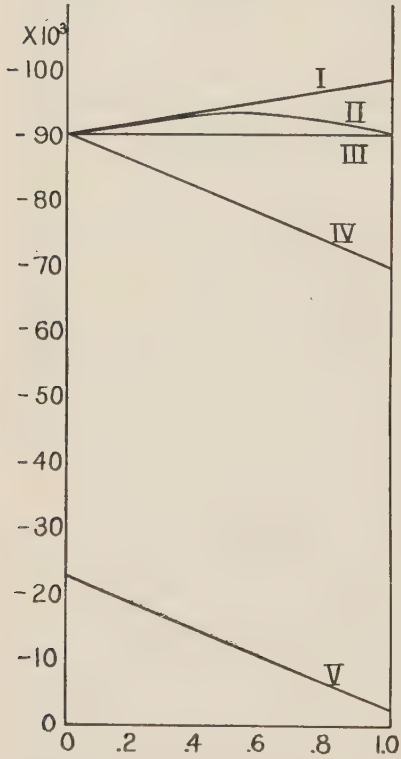

Fig. 14. Heat Content of Sulphuric Acid Solutions Referred to Varying Initial States

I. Lewis and Randall reference state

II. Curve for solution

III. Heat content water and acid reference state

IV. Heat content sulfur trioxide and water reference state

V. Heat content elements reference state

Bronsted gives a series of values for $\frac{\partial H}{\partial n_2}$ for sulphuric acid solutions of varying strengths and these are given in Table XLI. These results are plotted in Fig. 15 and the values for the area determined by counting squares.

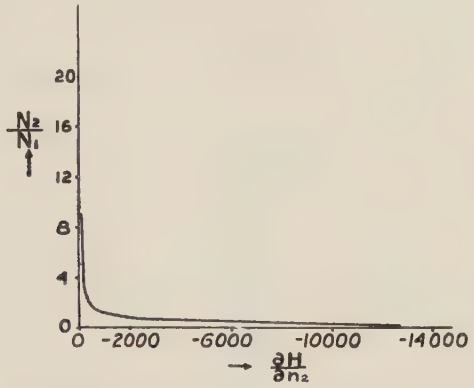

FIG. 15. Partial Molal Heat Content of Sulphuric Acid in Aqueous Solutions

TABLE XLI

PARTIAL MOLAL HEAT CONTENT OF SULPHURIC ACID SOLUTIONS

Mol. Fraction Acid—N_2	$\frac{N_2}{N_1}$	$\frac{\partial H}{\partial n_2}$	Mol. Fraction Acid—N_2	$\frac{N_2}{N_1}$	$\frac{\partial H}{\partial n_2}$
0.0001	.0001	− 20,050	0.45	.818	− 2960
0.01	.0101	− 17,250	0.50	1.00	− 1890
0.05	.0526	− 16,070	0.55	1.22	− 1160
0.08	.0870	− 14,260	0.60	1.5	− 670
0.10	.111	− 12,970	0.65	1.86	− 460
0.15	.175	− 10,890	0.70	2.33	− 290
0.20	.250	− 9,010	0.75	3.00	− 173
0.25	.333	− 7,520	0.80	4.00	− 102
0.30	.429	− 6,230	0.85	5.67	− 64
0.35	.539	− 5,070	0.90	9.00	− 47
0.40	.666	− 4,040	0.95	19.00	− 28

Table XLII gives the values obtained between the different concentrations. Column 2 gives differential values for $\frac{\partial H}{\partial n_1}$ between concentrations that differ by 0.05 from one another. Column 3 gives values for $\frac{\partial H}{\partial n_1}$ at varying values for N_2, assuming a value of − 8350 cals. for $\frac{\partial H}{\partial n_1}$ when $N_1 = 0$. Column 4 gives

similar values calculated by Brönsted and Column 5 values determined experimentally by Rumelin.[1]

TABLE XLII

HEAT CONTENT DATA FOR SULPHURIC ACID SOLUTIONS

Mol. Fraction Acid—N_2	Differential Values $\frac{\partial H}{\partial n_1}$	$\frac{\partial H}{\partial n_1}$ (calc.)	$\frac{\partial H}{\partial n_1}$ (Brönsted)	$\frac{\partial H}{\partial n_1}$ (Rumelin)
0.95	266	− 8161		
.90	124	− 7895		
.85	184	− 7771		
.80	248	− 7587		
.75	339	− 7339		
.70	364	− 7000		
.65	353	− 6636		
.60	617	− 6283		
.55	811	− 5666		
.50	973	− 4855	− 4850	
.45	801	− 3882	− 3880	
.40	620	− 3081	− 3060	
.35	560	− 2461	− 2470	
.30	490	− 1901	− 1910	− 1810
.25	434	− 1410	− 1450	− 1415
.20	399	− 976	− 1000	− 985
.15	297	− 577	− 580	− 630
.10		− 280	− 280	− 275

In the following table some values for heats of dilution are given for nitric, hydrochloric and oxalic acids.

TABLE XLIII

HEATS OF DILUTION

Mols. Water per 1 Mol. Acid	HNO_3	HCl	$C_2H_2O_2$
1	− 3340	− 5,370	+ 152
2	− 4860	− 11,360	+ 156
5	− 6760	− 14,960	
8	− 7220		
10	− 7270	− 16,160	
20	− 7360	− 16,760	− 173
50		− 17,100	− 278
100	− 7210	− 17,200	− 335
200	− 7180		− 375
300		− 17,300	

[1] *Z. physik. Chem.*, 58, 449 (1907).

The measurement of heats of dilution of solutions of electrolytes at extreme dilution has recently become a subject of renewed interest as an experimental method of investigating the theory of Debye and Hückel concerning strong electrolytes. The nucleus of this theory is the calculation of the potential of an ion in a medium of dielectric constant D when influenced by other ions. This is found to be [1]

$$\psi_i = \frac{Z_i \epsilon \kappa}{D} \tag{65}$$

where

$$\kappa^2 = \frac{4\pi\epsilon^2}{DkT} \sum n_i Z_i^2. \tag{66}$$

n_i being the number of ions of the ith kind per cc. and Z_i the valence of these ions. In what follows the discussion will be limited to uni-univalent ions. The above equation for the potential is a limiting law for great dilution. From this equation Debye and Huckel derived an expression for the electrical energy per cc. of ion solution

$$U_e = \tfrac{1}{2} n_i \epsilon Z_i \psi_i. \tag{67}$$

$$= \frac{\tfrac{1}{2} n_i \epsilon^2 Z_i^2 \kappa}{D}. \tag{68}$$

Debye [2] has also calculated the total electrical free energy to be gained by the complete separation of the ions from one another

$$-\Delta F = \sum \frac{\tfrac{1}{3} n_i \epsilon^2 Z_i^2 \kappa}{D} = \tfrac{1}{3} U_e. \tag{69}$$

The total heat of dilution from concentration c to zero concentration can be calculated from ΔF by means of the second law of thermodynamics

$$\Delta H = \Delta F - T \frac{d\Delta F}{dT},$$

$$\Delta H = + \frac{N\epsilon^2 \kappa}{D} \left(1 + \frac{T}{D} \cdot \frac{dD}{dT} \right). \tag{70}$$

Taking Drude's [3] value for the change of dielectric constant of water with temperature

$$\frac{dD}{dT} = -0.360,$$

$$\Delta H_{298} = -518\sqrt{C}, \tag{71}$$

which means that the heat of dilution should be directly proportional to the

[1] For the details of this calculation see Chap. XII, p. 788.

[2] *Physik. Z.*, **25**, 99 (1924).

[3] *Wied. Ann.*, **59**, 48 (1896).

square root of the concentration in the concentration range where the limiting law of Debye and Hückel is valid. Lange [1] and Nernst, Orthmann and Naude [2] have measured heats of dilution of strong electrolytes from 0.1 N concentration to zero. The work of Lange and Fajans appears to have been very carefully carried out and gives good support to the theory. The heat of dilution of five alkali halides was found to be negative (heat evolved on dilution) and for concentrations below 0.01 N the results obtained agreed quantitatively within the experimental error with those predicted by the theory. The nature of the results obtained is illustrated in Fig. 16.

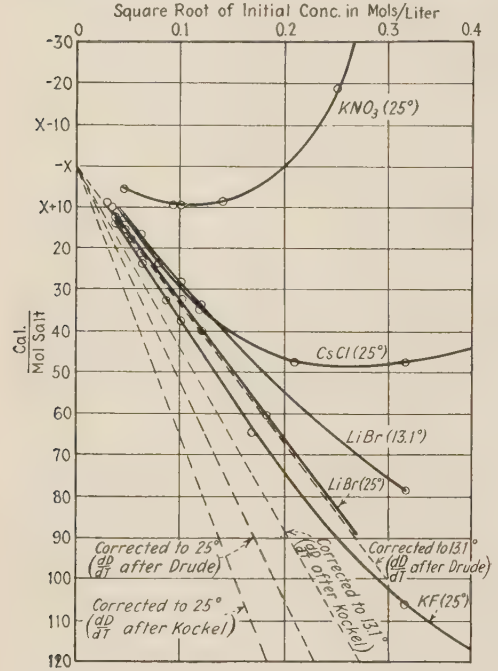

FIG. 16. Heats of Dilution at Low Concentrations

HEATS OF ADSORPTION

Since the amount of adsorption increases rapidly with decreasing temperature, it follows from the van't Hoff-Le Chatelier law that adsorption must be accompanied by a considerable evolution of heat. Favre,[3] Chappius,[4] Mond, Ramsay and Shields,[5] Dewar,[6] Titoff,[7] Lamb and Coolidge,[8] and Beebe and Taylor [9] have carried out quantitative investigations on heats of adsorption of gases on solids, mostly starting with the solid in an evacuated vessel and admitting the gas to atmospheric pressure. These measurements of the integral or total heat of adsorption are comparable to a heat of solution. The differential heats of adsorption obtained over small pressure ranges are more suitable to theoretical treatment and can be likened to a heat of dilution. A study of heats of adsorption has been of value in obtaining evidence concerning the nature of the centers of activity of a catalytic surface

[1] *Fortschritte Chem. Phys. and physik. Chem.*, 19, Heft 6, 1928.
[2] *Sitz. ber. preuss. Akad Wiss.*, 51 (1926); 136 (1927).
[3] *Ann. Chim. Phys.*, (5) 1, 209 (1874).
[4] *Wied. Ann.*, 19, 21 (1883).
[5] *Z. physik. Chem.*, 25, 657 (1898).
[6] *Proc. Roy. Soc.*, 74, 122 (1904).
[7] *Z. physik. Chem.*, 74, 641 (1910).
[8] *J. Am. Chem. Soc.*, 42, 1146 (1920).
[9] *J. Am. Chem. Soc.*, 46, 43 (1923).

It is possible to calculate heats of adsorption from a study of absorption isosteres. In this case the amount of gas adsorbed is constant and a study is made of the change in pressure in the gas phase with varying temperatures. Freundlich [1] gives a discussion of this method of calculating heats of adsorption. This type of calculation has been adversely criticised by Williams [2] but the objections have been critically examined by Coolidge [3] and found to be invalid.

Let us postulate a system the state of which is completely defined by two variables taken as temperature and pressure. For any reversible displacement in this system the increase in the energy of the system will be

$$dE = TdS - pdV,$$

where dS is the entropy change and p the external pressure. From this equation one readily derives the relationships

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T = -\frac{1}{T}\left(\frac{\partial q}{\partial V}\right)_T, \tag{72}$$

where ∂p is the heat absorbed. This relationship is certainly applicable to a system such as charcoal and vapor which has been found to be completely definable in terms of temperature and pressure. $(\partial p/\partial T)_V$ is the slope of the isostere, for constancy of volume implies constancy in concentration of the adsorption phase. On the other hand, if the volume changes isothermally, vapor will be desorbed in quantity sufficient to fill the new space and the accompanying heat absorbed will be the heat of adsorption per mol. (λ) times the concentration (mols. per c.c.) of the vapor at the given pressure which may be taken as equal to P/RT. We thus obtain the equation

$$\frac{\partial p}{\partial T}(\text{isosteric}) = \frac{p\lambda}{RT^2}, \tag{73}$$

which is an application of the Clausius-Clapeyron equation to heats of adsorption.

The data obtained by Coolidge for the heats of adsorption of a number of organic vapors on charcoal and those calculated from adsorption data are illustrated in Fig. 17. Circles correspond to directly measured heats and crosses are obtained from the slopes of the isosteres.

Lamb and Coolidge have found a relationship

$$h = mx^n \tag{74}$$

between the heat of adsorption, h, and the number of c.c. of gas adsorbed, x; m and n are constants for the vapor considered, and n is found to be nearly unity so that there is almost a linear relationship between heat of adsorption and amount of gas adsorbed. Coolidge in discussing the origin of the heat of adsorption believes that, in unsaturated systems, the heat is to be considered

[1] Colloid and Capillary Chemistry, Metheun and Co., p. 134.
[2] *Proc. Roy. Soc. Edinburgh*, **38**, 23 (1918).
[3] *J. Am. Chem. Soc.*, **48**, 1804 (1926).

as representing principally the work done by the attraction of the adsorbent plus the ordinary latent heat of condensation.

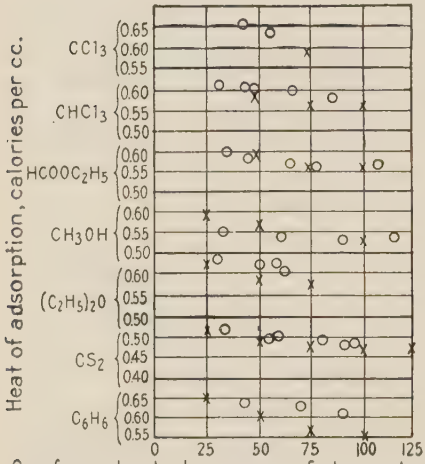

FIG. 17. Heat of Absorption of Organic Compounds on Charcoal

It is possible to express equation (73) in terms of the constants of the equation for the absorption isotherm.

$$\frac{x}{m} = \alpha p^{1/n} \tag{75}$$

where α and $1/n$ are constants for a given isotherm and x/m is the amount absorbed per gram at pressure p. Since we are working with x/m constant in this calculation

$$\frac{d \log p}{dT} = \left(\log \frac{x}{m} - \log \alpha \right) \frac{\partial n}{\partial T} - n \frac{d \log \alpha}{dT} \tag{76}$$

and

$$\Delta H = - RT^2(\zeta - \xi \log p), \tag{77}$$

where

$$\zeta = - \frac{d \log \alpha}{dT} \tag{78}$$

and

$$\xi = \frac{d \frac{1}{n}}{dT}. \tag{79}$$

and p is expressed in cm. of mercury. This equation has been tested by Titoff. He evaluated ζ and ξ through measurements of adsorption isotherms at different temperatures on coconut charcoal and determined the heat of adsorption, using an ice calorimeter. Table XLIV shows the agreement between the calculated and observed values. For Titoff's calculations $\frac{x}{m}$ is not constant, but the change in it is much smaller than in p and one can make a calculation employing a mean value of p.

TABLE XLIV

HEATS OF ADSORPTION ON CHARCOAL

Gas	ζ	ξ	ΔH (calc.)	ΔH (obs.)
Nitrogen	0.01367	0.00297	− 3875	− 4548
Carbon dioxide	0.01420	0.00477	− 6483	− 6514
Ammonia	0.02168	0.00987	− 7764	− 7928

The following table is due to Chappius.

TABLE XLV

HEATS OF ADSORPTION ON CHARCOAL

Gas	$\frac{x}{m}$ Before	$\frac{x}{m}$ After	p in Cm. Before	p in Cm. After	ΔH	Heat of Liquefaction
Air	0	7.44	0	70.47	− 2,400	
CO_2	22.6	44.1	8.22	36.32	− 7,300	− 6250
NH_3	105	131	12.25	22.25	− 8,100	− 5000
SO_2	70	90.6	7.06	45.1	− 10,900	− 5600
$CHCl_3$	62.2	72.3	17.48	67.54	− 10,700	

Variation of Heat of Adsorption with Pressure: As could be predicted from equation (77), the heat of adsorption decreases with increasing pressure.

TABLE XLVI

ADSORPTION OF AMMONIA ON MEERSCHAUM AT 0° C.

p in Cm.		$\frac{x}{m}$ Before	$\frac{x}{m}$ After	ΔH
Before	After			
0	0	0	24.2	− 20,500
0	0.5	24.2	48.3	− 12,700
0.5	3.71	48.3	72.3	− 11,300
2.93	21.50	72.3	95.3	− 8,970
21.50	57.56	95.3	117	− 7,600

For adsorption of gases on indifferent substances, the reaction concerned appears to be of a purely physical nature and the heat effect observed corresponds to the heat of vaporization and a heat of compression. It will be seen from Table XLV that the heat of adsorption is greater than the heat of liquefaction.

Dewar working at − 185° C. measured the integral heat of adsorption of several gases on charcoal.

TABLE XLVII

HEATS OF ADSORPTION ON CHARCOAL AT − 185° C.

Gas	ΔH	Heat of Liquefaction
H_2	− 1600	− 230
N_2	− 3686	− 1372
Ar	− 3636	
O_2	− 3744	− 1664
CO	− 3416	

Keyes and Marshall [1] have studied the variation in the heat of adsorption of oxygen on charcoal with the amount of gas adsorbed at 0° C. At zero concentration the heat of adsorption is $\Delta H = -72{,}000$ cals. and this falls off very rapidly with increasing concentration to a final constant value of $-4{,}000$ cals. per gram molecule adsorbed.

Blench and Garner [2] have studied this same heat of adsorption as a function of temperature for small quantities of oxygen adsorbed and their results are tabulated in Table XLVIII.

TABLE XLVIII

Heat of Adsorption of Oxygen on Charcoal

Temp.	18°C	199°	283°	450°
Heat of adsorp. in cals./g. mol.....	−52,000	−115,000	−154,000	−224,000

At the elevated temperatures the heat of adsorption is intermediate between the value for the heat of formation of carbon dioxide from solid carbon and oxygen (− 96,000 cals.) and that calculated for formation from carbon vapor and oxygen (− 241,000 cals.). Taylor has taken this result as a direct proof of the existence of highly unsaturated surface atoms in the carbon surface.

Mond, Ramsay and Shields [3] have measured the heat of adsorption of oxygen on platinum black and obtained a value of $\Delta H = -17{,}600$ cals. as compared with $\Delta H = -17{,}700$ cals. determined by Thomsen for the reaction

$$Pt + \tfrac{1}{2}O_2 + H_2O = Pt(OH)_2.$$

TABLE XLIX

Adsorption Isosteres for Hydrogen on Nickel

Cc. H_2 Adsorbed	p		$\frac{p_1}{p_2}$
	218°	184°	
6.7	88 mm.	17 mm.	5.18
6.9	128 "	24 "	5.33
6.1	34 "	6 "	5.66
			Av.....5.4

Beebe and Taylor determined the heat of adsorption for hydrogen on finely divided nickel and obtained values ranging from $\Delta H = -14{,}300$ cals. per mol. to $\Delta H = -20{,}600$, the larger value being for the poorer adsorbent. The differential heats of adsorption for hydrogen on nickel are constant for the

[1] *J. Am. Chem. Soc.*, **49**, 166 (1927).
[2] *J. Chem. Soc.*, **125**, 1288 (1924).
[3] *Z. physik. Chem.*, **25**, 657 (1898).

pressure range 0–760 mm., pointing apparently to a specific chemical action. A similar value to the above is obtained from the adsorption isosteres for hydrogen on nickel.[1]

Integrating the Clapeyron-Clausius equation, we obtain

$$\Delta H = 1.99 \times 2.303 \times \frac{T_1 T_2}{T_1 - T_2} \times \log \frac{p_2}{p_1} \cdot \qquad (80)$$

Inserting the above values, we obtain

$$\Delta H = -22{,}100 \text{ cals.}$$

The study of differential heats of adsorption enables one to determine the dependence of the heat of adsorption on the degree of saturation of the surface and ultimately to study the degree of saturation of the various surface atoms. Fryling[2] studied the differential heats of adsorption of hydrogen on pure

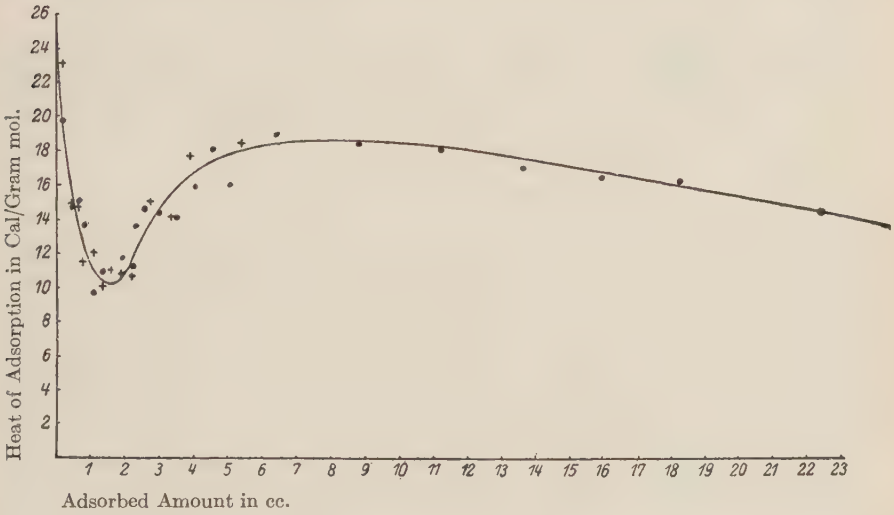

FIG. 18a. Heat of Adsorption of Carbon Monoxide on Copper

nickel and nickel containing up to 10 per cent thoria. For pure nickel the value gradually decreased from $\Delta H = -28{,}000$ cals. at 1 c.c. adsorbed to $-10{,}000$ cals. for the final value. For the promoted catalyst however the case was quite different; the heat of adsorption rose from an initial value of $\Delta H = -13{,}700$ cals. for 0.73 hydrogen adsorbed to a maximum value of $-32{,}500$ cals. at about 2 cc. adsorbed and then fell off again as with pure nickel. Fryling assumed the formation of atomic hydrogen in the initial stages of his experiment in order to explain the presence of a maximum in the curve. Taylor

[1] Gauger and Taylor, *J. Am. Chem. Soc.*, **45**, 920 (1923).
[2] *J. Phys. Chem.*, **30**, 818 (1926).

and Kistiakowsky [1] have found similar results in the case of the adsorption of hydrogen and carbon monoxide on copper. Their experimental arrangement was more sensitive than that of Fryling and it is certain that the copper used was free from oxide. Fig. 18 illustrates the nature of the results obtained. Taylor and Kistiakowsky assumed that in simple cases the whole of the potential energy of adsorption is set free as heat but if this energy is

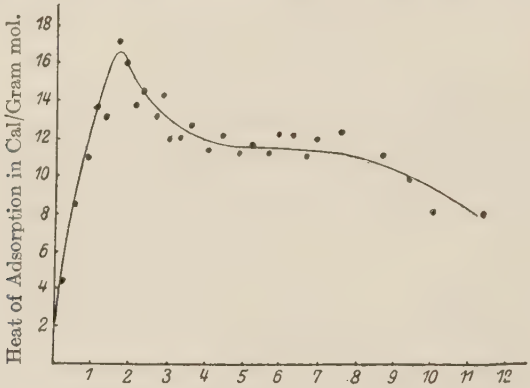

FIG. 18. Heat of Adsorption of Hydrogen on Copper

great enough it is possible for some of it to be used in activating the molecules adsorbed. The maximum in the curve for hydrogen is explained by assuming that hydrogen adsorbed by the most unsaturated surface atoms is activated and only a small portion of the potential energy of adsorption appears as heat; at later stages in the adsorption there is no storing up of energy by activation and thus there is an increase in the heat evolved. This point of view has been questioned by Polanyi [2] and by Herzfeld.[3]

Heat of Wetting: The heat of wetting is the heat absorbed when a solid surface and a liquid surface are brought together. It is the same quantity as the integral heat of adsorption of a vapor at its saturation pressure, and could be determined with greater accuracy experimentally by observing this quantity. Parks [4] has shown that the amount of heat absorbed is proportional to the surface. Schwalbe [5] has shown that the heat of wetting of hydrated silica is negative above 4° C. and positive below that temperature. These experiments support the idea that there is a direct connection between adsorption and compressibility. Gaudechon [6] obtained the data in Table L for different adsorbents and liquids. The powders were dried at 100° C.

[1] *Z. physik. Chem.*, **125**, 353 (1927).
[2] *Z. physik. Chem.*, **132**, 371 (1928).
[3] *J. Am. Chem. Soc.*, **51**, 2609 (1929).
[4] *Phil. Mag.*, (6) **4**, 240 (1902).
[5] *Drud. Ann.*, **16**, 32 (1905).
[6] *Compt. rend.*, **157**, 209 (1913).

TABLE L

HEAT OF WETTING FOR 1 G. ADSORBENT IN GRAM CALORIES

Liquid	Adsorbent		Sugar Char
	Alumina	Quartz	
Water	− 12.6	− 15.3	− 3.9
Methyl alcohol	− 11.0	− 15.3	− 11.5
Ethyl "	− 10.8	− 14.7	− 6.9
Propyl "	− 10.2	− 13.5	− 5.6
Amyl "	− 10.1	− 13.5	− 3.7
Formic acid	− 12	− 14.5	− 12
Acetic "	− 9.3	− 13.5	− 6.0
Acetone	− 8	− 13.5	− 3.6
Carbon tetrachloride	− 1.8	− 8.1	− 1.5

The action of water vapor on dried cotton wool [1] is very interesting. If the bulb of a thermometer be covered with carefully dried cotton wool and then dipped in water at the same temperature, the thermometer will rise 8°–12°.

[1] Masson, *Proc. Roy. Soc.*, 74, 230 (1904).

CHAPTER VII

THE LAWS OF DILUTE SOLUTIONS

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The present chapter is devoted to a consideration of those generalizations which have been found to exist between the magnitude of certain (colligative) properties common to all solutions and the effect on these properties of changing composition of the solution. While the relations that exist among these properties for a given solution are such that, knowing the magnitude of one, under fixed temperature and pressure conditions, the others may be calculated by the use of the principles of thermodynamics, the effect of changing composition is much more complicated, and while the general effect of changing composition is qualitatively the same in all cases, this effect is by no means capable of the same exact mathematical treatment as are the mutual relations existing among the other properties of solutions alluded to above. It will, therefore, be necessary to realize that the application of thermodynamics to the colligative properties of solutions is capable of concise statement only in such cases where the effect of changing composition on these properties is capable of quantitative expression, i.e., in the case of the so-called "perfect" or "ideal" solutions.

A perfect solution is one in which the volume change accompanying a small dilution is additive, and no effect is noted other than the alteration of the volume of the solution, similar, in a way, to the change of volume of a perfect gas when it expands into a vacuum. The absence of any heat effect on dilution is a good criterion that a solution is ideal. The deviation of a solution from ideality depends on the nature of the constituents of the solution, the solute and solvent, and on the concentration of the solution. Increased dilution, in general, causes all solutions to approach the ideal condition, the nature of the components determining to what extent dilution must be increased before ideal conditions are realized. This range of concentration over which the relations derived for ideal solutions may be expected to hold will, therefore, vary with the nature of the individual substances concerned. In many cases, it will be found that perfect solutions are not realized at greater concentration than 0.01 M (in some cases at much smaller concentrations), while for some, practically perfect solutions may be formed at much greater concentrations. In order to treat the subject in a general way, it will be necessary to limit consideration to perfect solutions, so that the present chapter is limited to a discussion of *dilute* solutions formed when only two substances are present in the

solution. In order to simplify the conditions as much as possible, it is further assumed that only one of these constituents is volatile and the vapor phase is composed of molecules of this constituent only.

Definition: A solution is a one-phase system consisting of two or more molecular species not transformable one into the other. It is, therefore, a homogeneous physical mixture of the various molecular species in question. Not every pair of substances will form a solution to a noticeable extent when they are brought in contact, and the extent to which they will mix to form such a solution will vary greatly with the nature of the substances concerned. Further, as we shall see, the extent to which solution takes place is so varied that substances ordinarily considered insoluble will show, on close inspection, some evidence of solubility. Our ideas of soluble and insoluble substances are therefore relative. For example, water and mercury, when shaken together, will soon separate as a two-phase system and the mixture is not a solution. Water and alcohol, on the other hand, will form a single-phase system when they are mixed in any proportions whatever. These two pairs of liquids represent qualitatively the extremes as regards solubility. Others, such as water and benzene, occupy an intermediate position as regards solubility, and will usually give rise to a two-phase system. Each phase will be found homogeneous and will contain a measurable amount of each constituent. One phase will contain a small amount of water dissolved in a large amount of benzene; the other will contain a small amount of benzene dissolved in a large amount of water. Each phase is, therefore, a solution according to the above definition. In most cases, especially solid-liquid mixtures, solution occurs only to a limited extent, as in the case of sugar and water, and the solution is said to be saturated (when this limit is reached).

From the recent work of Baker [1] it is not unreasonable to expect that solution actually may take place to a limited extent in many cases where the substances are usually regarded as insoluble, but the amount required to produce saturation is so small that it is measurable only indirectly by the change produced in certain properties of the pure solvent. For instance, water is not regarded as soluble in mercury, but by taking extreme care to remove all traces of water from mercury, Baker has found the boiling point of the mercury may be raised considerably above its ordinary boiling point. We should therefore realize that solubility is a universal property of all substances varying in extent from an immeasurably small, though effective, amount to an infinitely great amount. In general, the more closely the constituents are related chemically, the greater will be their mutual solubility. However, this has no bearing on the definition of a solution as given above. Mercury may not be capable of dissolving water to a measurable extent but the small amount taken up would be a solution of water in mercury. In the same way water and benzene mutually dissolve to only a limited extent, giving a two-phase system, each phase being a solution.

If this two-phase system water-benzene is shaken or stirred vigorously,

[1] *J. Chem. Soc.*, **121**, 568 (1922).

the phases may be further dispersed, but the result is not a homogeneous phase, nor do the benzene and water remain dispersed after agitation ceases; separation of the two original phases begins and the system soon returns to its original condition with its two phases completely separated. In many cases, when two substances are mechanically dispersed, separation is much slower and may give the impression of permanence; when the dispersion is brought about under the proper conditions and to a sufficient extent, the separation of the constituents of the mixture into two clearly defined phases is so extremely slow that the appearance of permanence is very deceptive. Nevertheless, with sufficient time and care in the examination of such cases, it can usually be shown that separation is actually in progress and the dispersion is not permanent. Such solutions are known sometimes as pseudo-solutions or more generally as "Colloidal Solutions." Such cases do not come within the definition of solutions given above. They are neither molecularly dispersed systems nor *permanent*, and, hence, may not be treated in the same comprehensive way as true solutions. In addition to the condition that a solution contains its constituents molecularly dispersed as a homogeneous phase, the system once produced is permanent. It will therefore form spontaneously when the constituents are brought into material contact. This is a fundamental distinction, since, like all processes which occur spontaneously without the application of outside influences, it may be made, by use of a suitable mechanism, to yield a certain amount of useful work, or, conversely, such a solution having once been produced, a definite amount of work must be expended to separate its constituents. The calculation of the maximum work so obtainable makes possible the application of thermodynamics to the study of solutions. This clearly differentiates solutions from such colloidal solutions where the natural change is in the reverse direction. For example, a colloidal solution may be formed, but careful observation (color change, change of viscosity, etc.) shows that the system is undergoing change and, finally, the change progresses to such a degree that close inspection reveals a lack of homogeneity. Colloidal solutions contain constituents highly dispersed in one another; they are not molecularly dispersed, however,[1] and are intermediate between true solutions and coarse suspensions that are evidently heterogeneous.

Reference has been made above to the constituents of a solution. By this term is meant any one of the pure chemical substances whose molecular dispersion results in the formation of a solution. With the exceptions noted below, each chemical substance furnishes but one kind of molecule and the constituents of a solution indicate the different molecular species which occur in a solution. Associated substances, such as water, and many other oxygen compounds such as the alcohols, are recognized as pure substances since, while they furnish more than one molecular species (water, for example, being an

[1] Zsigmondy's colloidal gold has been shown by Scherrer (*Kolloidchemie*, Zsigmondy, p. 405, Fourth Edition, Leipzig, 1922) to consist of particles containing 380 atoms. Such particles are small, viewed from the standpoint of colloid chemistry; they are evidently far from being molecularly dispersed.

equilibrium of the molecular species H_2O, $(H_2O)_2$, $(H_2O)_3$ and perhaps others), this equilibrium is established so rapidly that there is no experimental evidence of water having variable properties under the same conditions. Such substances are treated as pure substances having the molecular composition of the vapor phase; in the case of water, as being composed of H_2O molecules, since this is the molecular composition of the vapor phase.[1]

Classification: The three physical states of matter, solid, liquid and gaseous, which we have in the case of pure substances, extend also to solutions so that this subdivision of solutions is both natural and convenient.

Gaseous Solutions: In the case of gaseous solutions the molecules are so far apart that, in the absence of chemical action, they are in most cases practically without influence on each other, as shown by the absence of heat effects on mixing and the relatively small effect when they are allowed to expand into a vacuum. Under such circumstances the physical properties are related to those of the constituents in the simplest way. In the first place, owing to the small mutual attraction of molecules in the gaseous condition, gases mix in all proportions to form true solutions. It is not surprising to find that in gaseous solutions each constituent retains its physical properties unchanged and most of the physical properties of such solutions are therefore additive and may be expressed simply as the sum of the magnitudes of each constituent with respect to the property in question.

Thus, if we consider the magnitude P of any such property of a gaseous solution, it may be simply expressed as follows:

$$P = P_{0A}N_A + P_{0B}N_B + \cdots,$$

where P_{0A}, P_{0B}, $\cdots$ are the magnitudes per mole of the gases A, B, $\cdots$ and N_A, N_B, $\cdots$ are the moles of the individual molecular species A, B, $\cdots$ present in the solution. Dalton's law of partial pressures is an illustration of the application of this relation. Other physical properties may be similarly expressed. The properties of gaseous solutions may be treated satisfactorily by the application of the gas laws and the above relationship.

Solid Solutions: In certain cases two solids may form physical mixtures that are homogeneous and therefore must be classed as solutions. As examples of this type of solution there are certain mixed crystals and certain alloys.[2] Equilibrium in such systems is reached with great slowness and, consequently, measurements are made very uncertain on account of the uncertainty as to what represents the true state of equilibrium. The laws of solutions may be applied here only as an approximation. The same is true to a large extent in certain cases of liquid solutions with high viscosity.

Liquid Solutions: Liquid solutions are by far the most important as most chemical reactions are brought about in liquid solutions both in the laboratory and in nature. An enormous amount of work has been done in order to gain a knowledge of the physical behavior of the constituents of liquid solutions as

[1] Kendall, *J. Am. Chem. Soc.*, **42**, 2477 (1920). Menzies, *ibid.*, **43**, 851 (1921).

[2] van't Hoff, *Z. physik. Chem.*, **5**, 322 (1890).

this must form the basis for the interpretation of the conduct of these constituents under all circumstances. Practically all that follows is therefore written from the standpoint of such solutions.

Composition of Solutions: Mention has already been made of the constituents of a solution, meaning thereby the chemical substances the intermingling of whose molecules forms the solution. Thus, sugar, when brought in contact with water, dissolves and continues to exist as sugar in the solution, from which the sugar may be recovered unchanged. Sugar and water are here the constituents of the solution and the molecules of sugar and the molecules of water are the molecular components of the solution. An arbitrary distinction is nearly always made between the constituents, chiefly on account of the fact that in most cases the solubility is limited. Thus, in the case of sugar and water, solution will take place only to a limited extent and the solution is then said to be saturated. When this occurs, there will be an excess of water in the solution but little if any of the water will dissolve in the excess sugar. Water is said to have a solvent action on sugar and water is referred to as the solvent and sugar as the dissolved substance or solute. These terms are used in this way generally for solutions formed from liquids and either gases or solids, the liquid constituent being termed the solvent and the other constituent the solute. In many cases, especially when dealing with two liquids, the distinction is quite arbitrary. For example, water and alcohol mix in all proportions and the distinction between solute and solvent might be reversed or lose its significance. Again, two liquids, such as benzene and water, form two layers in which the relative quantities of the two constituents are reversed. In such cases the solvent is usually the constituent present in larger quantity. This distinction of solvent and solute is largely for convenience as there is no theoretical distinction, except that, in dilute solutions, the solvent is practically a continuous phase in which the solute is molecularly dispersed. We could therefore distinguish the two constituents of a solution on this basis as the continuous and dispersed constituents.

Method of Expressing Composition of Solutions: The early method of expressing composition in terms of the percentages by weight of the various constituents of a solution, though convenient for analytical purposes, is nevertheless unsuited for theoretical considerations. As we shall see later, the properties of solutions which we shall consider are determined, not by the relative weights of the substances present, but rather by the relative number of molecules of the constituents present in the solution. Such properties of solutions have been designated by Ostwald as colligative properties. It is therefore evident that the logical and convenient method of expressing the composition of a solution is in terms of gram molecular weights or moles. This method of expressing composition shows its value, as we have seen, in expressing the physical properties of gaseous solutions. The mol-fraction method of expressing the composition of solutions is explainable as follows: if a solution is composed of N_A gram moles of constituent A and N_B gram moles of constituent

B, the mol-fraction for the constituent A would be $\frac{N_A}{N_A + N_B}$ and for the constituent B, $\frac{N_B}{N_A + N_B}$. The expressions $\frac{N_A}{N_A + N_B}$ and $\frac{N_B}{N_A + N_B}$ are usually written X_A and X_B respectively. X_A and X_B are then the mol-fractions of the respective constituents, or the amount per unit of solution. The amount of a substance may be expressed in moles, equivalents or formula weights per liter of solution. Another system expresses these same quantities in terms of 1000 grams of solvent instead of 1000 cc. of solution. Concentrations expressed in terms of 1000 cc. of solution and using the above methods of expressing the amounts of substances are known as molal, formal or normal concentrations. When 1000 grams of solvent is made the basis of calculating concentration, we have the composition expressed as weight-molal, weight-formal or weight-normal concentration.

The method of expressing the composition of solutions in terms of molal concentrations would be preferable provided we had a satisfactory kinetic expression for the colligative properties of solutions; while there undoubtedly is a kinetic basis for these phenomena, it has not yet been possible, owing to the complexity and changing nature of solutions with changing conditions, to obtain a general kinetic expression for the behavior of solutions. The effect of composition of solution on the colligative properties can be best expressed as a function of the mol-fraction composition, and, for this reason, this method of expressing the composition of solutions is used in the following discussion.

Colligative Properties

Let us now consider the interrelationships existing between the various colligative properties of solutions—vapor pressure, boiling points, freezing points and osmotic pressure. The quantitative relationship existing among these properties is, as stated at the beginning of this chapter, such that, starting with an expression for any one of them, we are able to derive expressions for the others. These expressions, including the effect of composition, cannot all be derived on a purely thermodynamic basis. We must start with some empirical fact (the experimental basis of which, however, leaves us no concern as regards its validity), on the basis of which we derive an expression for the property in question and from which, in turn, we are able by purely thermodynamic reasoning to develop the expressions for the other properties. The development of a theory of solutions begins with the work of van't Hoff [1] who indicated the analogy existing between the laws of solutions and those of gases. The existence of this analogy has led to the conception of a kinetic basis for the treatment of the subject which we shall first consider. Though van't Hoff merely indicated the kinetic origin of osmotic pressure in a qualitative way,

[1] *Z. physik. Chem.*, 1, 181 (1887); Ostwald's Klassiker, No. 110; J. H. van't Hoff, Sein Leben und Werken, by E. Cohen, Leipzig, 1912; *Ber.*, 27, 1 (1894).

a complete kinetic theory of dilute solutions has been developed by other investigators.[1]

In the following section we shall discuss the elementary considerations of the laws of dilute solutions.

Vapor Pressure Lowering: If we consider a liquid and its vapor above it, there must exist a definite relationship between the distribution of any definite molecular species between the two phases, liquid and vapor. Since the pressure of a gas is proportional to the number of particles present per unit volume, the vapor pressure of a liquid due to any molecular species present will be proportional to the number of particles of this molecular species present in the liquid. Expressed mathematically,

$$p = kx_0,$$

i.e., the vapor pressure of a liquid, p, is proportional to x_0, the mol-fraction of the liquid existing in the form of the molecular species which gives rise to the vapor pressure, p. If we consider a pure liquid in which the same molecular species exists in both the liquid and vapor phase,[2] this fraction x_0 becomes equal to unity, and k, the proportionality factor, equals the vapor pressure of the pure liquid which we may express by p_0. Our equation then becomes

$$p = p_0 x_0,$$

which is the simplest expression of Raoult's law [3] for vapor pressure lowering and states that the vapor pressure of a solution is proportional to the mol-fraction of the solvent present in the solution. As is evident from the above considerations, p is the vapor pressure due to a definite molecular species present to the extent of the fraction x_0 in the solution and does not indicate, for example, the vapor pressure that would result if the molecules of the solvent in the vapor phase were dissociated. Subtracting both sides of the above equation from p_0 and dividing by this term, we obtain the expression

$$\frac{p_0 - p}{p_0} = x = \frac{N}{N_0 + N},$$

where x will be the mol-fraction of the solute present in the solution. The term, N, refers to the moles of solute present, having the molecular weight of the solute in the solution, while N_0 is the number of moles of solvent present having the molecular weight of the solvent in the vapor state.

Henry's Law: Raoult's equation developed above deals with the vapor pressure of the solvent only. We have, by a more general application of the

[1] L. Boltzmann, *Z. physik. Chem.*, **6**, 474 (1890); **7**, 88 (1891); E. Riecke, *ibid.*, **6**, 564 (1890); H. A. Lorentz, *ibid.*, **7**, 36 (1891); L. Natanson, *ibid.*, **30**, 681 (1899); M. Reinganum, *Boltzmannfestschrift*, Leipzig, 1904; G. Jaeger, *Wien. Ber.*, (IIa) **22**, 979 (1913); P. Langevin, *J. Chim. Phys.*, **10**, 524 (1912).

[2] In the case of a solvent like water, where we have an equilibrium in the liquid phase between the molecular species as represented by the relation $(H_2O)_3 \rightleftharpoons (H_2O)_2 \rightleftharpoons (H_2O)$, it can be shown, from the mass action law, that the same relationship is true.

[3] Raoult, *Compt. rend.*, **104**, 1430 (1887); *Z. physik. Chem.*, **2**, 353 (1888).

principle underlying Raoult's law, an expression for the vapor pressure of a volatile solute (gas) in a solution, which expression is known as Henry's law. This law states that the vapor pressure of any chemical substance present in a solution is proportional to its mol-fraction or

$$p = kx,$$

where k is a proportionality constant. Since the vapor pressure of a substance is merely a measure of its concentration in the vapor state, we can express Henry's law for dilute solutions of gases in liquids in the form

$$c/p = k,$$

which states that the distribution of a gaseous substance between the liquid and gaseous phases is a constant. In this equation, c represents the concentration of the dissolved substance $\left(\text{since } \frac{N}{N_0 + N} \text{ for very dilute solutions is substantially equal to } \frac{N}{N_0} \text{ or the concentration } c\right)$, and p the vapor pressure corresponding to this concentration.

Henry's law has been rigidly investigated over a wide pressure range to determine the extent of its applicability.[1] Sackur and Stern have shown that in the case of carbon dioxide in various organic liquids the behavior of the dissolved carbon dioxide is more nearly in accord with the ideal laws than that remaining in the gaseous condition. In expressing Henry's law, it has also been found that a greater constancy of the coefficient, k, is obtained if we use Ostwald's coefficient for expressing solubility. In this system, we express k as the ratio of the concentration in the solution and in the gas phase, employing data for the density of the solution.

Distribution Law: An expression for the distribution of a substance between two non-miscible solvents can be derived from Henry's law. If a substance whose concentration is C_A in the liquid A has a vapor pressure p, then according to Henry's law

$$\frac{C_A}{p} = k_1.$$

Similarly, if its concentration in the liquid B is C_B, since the partial pressure p must be the same over both phases,

$$\frac{C_B}{p} = k_2$$

and

$$\frac{C_A}{C_B} = \frac{k_1}{k_2} = k,$$

[1] Sander, *Z. physik. Chem.*, **78**, 513 (1912). Sackur and Stern, *Z. Elektrochem.*, **18**, 641 (1912).

which states that the distribution of a substance between two non-miscible solvents is constant, at any definite temperature, regardless of the initial concentrations employed.

This same relationship also follows from the perpetual motion principle which may be applied by a consideration of the conditions shown in the accompanying diagram (Fig. 1). If we have two immiscible liquids, A and B, in which a volatile substance is dissolved at some definite temperature, the partial vapor pressure of this substance must, at equilibrium, be the same over A and B, for, otherwise, perpetual motion would result by the movement of the vapor from the region of higher to lower vapor pressure where, due to the disturbance of the existing equilibrium, it would dissolve, pass into the second liquid and so maintain a difference in vapor pressures. Perpetual motion being assumed, as a result of experience, to be impossible, the vapor pressure of the dissolved substance must, therefore, be the same over both liquids.

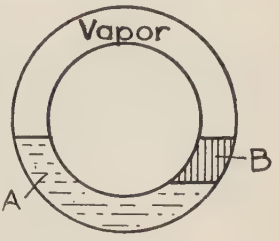


FIG. 1

This method of proof, due to Ostwald, can be similarly applied to a great number of other cases. In general, it can be applied to show that if any two phases are both in equilibrium with a third phase, they are in equilibrium with each other.

By a similar consideration, Ostwald has shown that osmotic pressure must be independent of the type of membrane used, regardless of the mechanism of the process of osmosis.

As is evident from its method of derivation, the relationship, $\frac{C_A}{C_B} = k$, for the distribution of a substance between two phases, A and B, is only valid if the substance has the same molecular structure in both phases. If, however, it exists as the simple molecule, M, for example, in the phase A, and as an associated molecule $(M)_n$ in the phase B, a corresponding relation can be derived.

If we represent the process of association by the equation

$$nM = (M)_n,$$

it follows, from the mass action law, that

$$\frac{(M)_n}{(M)^n} = K \qquad \text{and} \qquad (M) = \sqrt[n]{\frac{(M)_n}{K}}.$$

If we then express the concentration of the substance (M) in terms of its associated form $(M)_n$, we obtain

$$\frac{C_A}{\sqrt[n]{\frac{(C_B)}{K}}} = k,$$

where C_A will be the concentration of the non-associated form in the phase A, and C_B the concentration of the substance in the phase B, where it is associated and has a molecular weight n times that in A. Combining the two constants, we obtain

$$\frac{C_A}{\sqrt[n]{C_B}} = K',$$

which is our desired relationship.

Raising of the Boiling Point: The boiling point of a liquid being defined as the temperature at which its vapor pressure equals the opposing pressure of the atmosphere, it follows that the boiling point of a pure liquid must be raised by the addition of a non-volatile solute, since this brings about a lowering of its vapor pressure. We can derive the relation between this increase in boiling point with decreasing vapor pressure by considering the effect of temperature on the vapor pressures of solvent and solution as in the accompanying diagram in which the curves AC and DG (congruent for dilute solutions) represent the change of vapor pressure, with temperature, of solvent and solution respectively. The abscissæ of the points B and E will be their respective boiling points, under a pressure, P_0, equal to 760 mm. of mercury, which we shall denote by the symbols T_0 and T. Considering the geometrical relationships of the figure over an infinitesimal range, in which case the curves may be treated as straight lines, we have

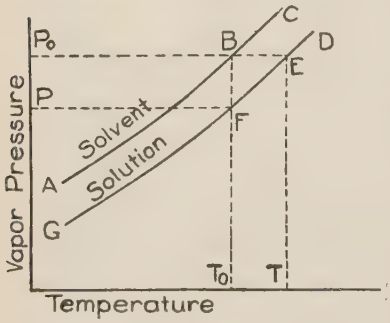


FIG. 2

$$\frac{BF}{BE} = \frac{p_0 - p}{T - T_0} = \tan \angle BEF = \text{slope of curve } DG.$$

Since the curves may be considered as parallel over a small range, the fraction $\frac{p_0 - p}{T - T_0}$ is also the slope of the curve AC. Expressed in terms of differentials, this gives

$$\frac{dp_0}{dT_0} = \frac{p_0 - p}{T - T_0},$$

and, substituting for $p_0 - p$ its value $p_0 x$ in Raoult's equation so as to introduce the effect of concentration, we obtain

$$T - T_0 = \frac{p_0}{\frac{dp_0}{dT_0}} x,$$

or

$$\Delta T = B_0 x = B_0 \frac{N}{N_0 + N},$$

which, for dilute solutions, becomes

$$\Delta T = B_0 \frac{N}{N_0}.$$

This equation states that the rise in boiling point of a solution is proportional to the mol-fraction of solute present. The constant B_0, known as the boiling-point constant, represents the relation between the vapor pressure of the solvent and the change in vapor pressure of the solvent with temperature and may be calculated from these, or from its equivalent in the approximate Clapeyron-Clausius' equation

$$\frac{\frac{dT_0}{dp_0}}{p_0} = \frac{RT_0^2}{\Delta H},$$

in which ΔH denotes the molal heat of vaporization of the solvent at its boiling point, T_0. B_0 also denotes the boiling-point rise per mole of solute in one mole of solvent and may thus be directly determined. Instead of this constant, the molal boiling-point constant which refers to the rise in boiling point produced by 1 mole in 1000 grams of solvent is usually recorded and used in the literature.

The Lowering of the Freezing Point: The fact that solutions (sea water for example) freeze at a lower temperature than the pure liquids has long been observed. Blagden[1] first showed that the lowering of the freezing point was proportional to the concentration and this relationship is therefore referred to as Blagden's law. Just as in the case of the boiling point, we can arrive at a relation between the vapor pressures and freezing points of solvents and solutions, and, by applying the Raoult relation between vapor pressure lowering and concentration, express the lowering of the freezing point in terms of the concentration of the dissolved substance.

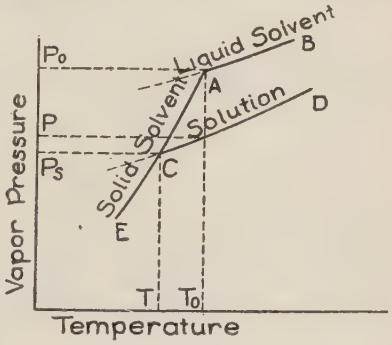


FIG. 3

The freezing point of a solution is defined as that temperature at which the solid solvent can exist in equilibrium with the solution. If we represent the change of the vapor pressure of a pure liquid solvent, solid solvent, and its solution as in the accompanying diagram (Fig. 3), we can derive a relationship

[1] *Phil. Trans.*, 78, 277 (1788). Ostwald's Klassiker, No. 56 (W. Engelmann, Leipzig, 1894).

by geometrical considerations as was done above in the case of the boiling point. AB represents the vapor pressure of pure solvent, CD that of the solution in which the mole-fraction of solute is x and AE that of the solid solvent. The intersection points, A and C, of the last curve with the others are the freezing points of solvent and solution respectively.

It is evident from geometrical considerations of the figure that

$$\frac{P_0 - P_s}{T_0 - T} = \frac{\partial P_{\text{solid}}}{\partial T}, \tag{1}$$

where $\frac{\partial P_{\text{solid}}}{\partial T}$, the slope of the curve for the solid solvent, gives the change in vapor pressure of the solid solvent with temperature. Also,

$$\frac{P - P_s}{T_0 - T} = \frac{\partial P_{\text{solution}}}{\partial T}, \tag{2}$$

where $\frac{\partial P_{\text{solution}}}{\partial T}$, the slope of the solution curve, gives the change in vapor pressure of the solution with change of temperature. If we assume that the vapor pressure curves for solution and liquid solvent are parallel, i.e.,

$$\frac{\partial P_{\text{solution}}}{\partial T} = \frac{\partial P_{\text{solvent}}}{\partial T},$$

we obtain, by subtracting (2) from (1),

$$\frac{P_0 - P}{T_0 - T} = \frac{\partial P_{\text{solid}}}{\partial T} - \frac{\partial P_{\text{solvent}}}{\partial T}. \tag{3}$$

In order to derive a relation between the freezing-point lowering and mole-fraction analogous to the relation for the rise in boiling point, we must apply the approximate Clapeyron equation, which gives the expressions for the temperature coefficients of the vapor pressures of the solid and liquid solvents:

$$\frac{\partial P_{\text{solid}}}{\partial T} = \frac{\Delta H_s P}{RT^2},$$

where ΔH_s is the molal heat of vaporization of the solid solvent, and

$$\frac{\partial P_{\text{solvent}}}{\partial T} = \frac{\Delta H_l P}{RT^2},$$

where ΔH_l is the molal heat of vaporization of the liquid solvent. Hence,

$$\frac{\partial P_{\text{solid}}}{\partial T} - \frac{\partial P_{\text{solvent}}}{\partial T} = \frac{(\Delta H_s - \Delta H_l)P}{RT^2},$$

where $\Delta H_s - \Delta H_l$ will be the molal heat of fusion, ΔH_0, of the solid solvent. We may therefore write equation (3) as

$$\frac{P_0 - P}{T_0 - T} = \frac{\Delta H_0 P}{RT^2}.$$

Substituting for $\frac{P_0 - P}{P}$ its value in the Raoult equation, we obtain

$$T_0 - T = \frac{RT^2}{\Delta H_0} x \qquad \text{or} \qquad -\Delta T = k_F x,$$

which is our desired relationship.

Osmotic Pressure: The process of osmosis was first observed by Abbé Nollet,[1] who showed that if a solution of sugar be placed in a vessel which is closed below by an animal membrane and dipped in a vessel of water, the latter will diffuse through the membrane and cause the solution to rise in the containing vessel. The phenomenon may be illustrated by the use of the apparatus shown in the accompanying diagram (Fig. 4). A glass vessel *A* which has a long narrow tube attached to it (a thistle tube serves the purpose) is closed at the bottom by a piece of parchment paper, *C*, filled with a sugar solution and supported in a vessel of water. The column of liquid in the tube, *B*, will be seen to rise until the hydrostatic pressure produced just counter-balances the force tending to cause water to enter the vessel. This pressure is known as the osmotic pressure and is caused by the force tending to bring about equilibrium between the pure solvent and solution which in the absence of a membrane results in mixing by diffusion and the production of a homogeneous solution. Osmotic pressure is, then, the excess pressure which must be put on a solution to bring it into equilibrium with the solvent. Between 1826 and 1848 Dutrochet[2] and Vierodt[3] made some quantitative measurements using pigs' bladders as semi-permeable membranes and first recognized the significance of osmotic pressure in physiological processes. Moritz Traube,[4] following the analogy in behavior shown by Graham[5] to exist between animal and colloidal substances, first showed that certain inorganic precipitates of a colloidal nature could act as semi-permeable membranes. Pfeffer[6] first carried out a series of reliable quantitative measurements using porous clay cells in the pores of which was deposited a membrane of $Cu_2Fe(CN)_6$. The modern work of Morse

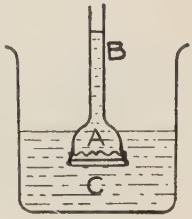


FIG. 4

[1] Recherches sur les causes de Bouillonement des Liquids, Paris, 1748.

[2] *Ann. Chim. Phys.*, [2] **35**, 393 (1827); [2] **37**, 191 (1828); [2] **49**, 411 (1832); [2] **51**, 159 (1832).

[3] *Ann. Phys.*, [2] **73**, 519 (1848).

[4] *Arch. f. Anatomie u. Physiologie*, 1867.

[5] *Phil. Trans.*, **144**, 177 (1854).

[6] *Osmotische Untersuchungen*, Leipzig, 1877.

and Frazer and their students [1] in America, of the Earl of Berkeley and of Hartley [2] in England, and that of other workers [3] have supplied experimental data which have served as a basis for theoretical treatment.

The theoretical treatment of osmotic pressure began with van't Hoff [4] who made use of the experimental data obtained by Pfeffer to confirm his generalizations. Van't Hoff showed that there exists an analogy between the osmotic pressure of a dilute solution and the gaseous pressure that the solute would exert if it existed in the form of a gas in the volume occupied by the solution. As will be seen from the data of Table I obtained by Pfeffer for

TABLE I

THE OSMOTIC PRESSURE OF SUCROSE (PFEFFER)

Concentration in Per Cent	Osmotic Pressure in Atmospheres	Ratio of Osmotic Pressure to Concentration
1	0.686	.68
2	1.34	.67
4	2.75	.68
6	4.04	.67

sugar solutions, osmotic pressure is directly proportional to concentration, a relation corresponding to Boyle's law for gases. Moreover, the change in osmotic pressure with temperature, as van't Hoff showed from Pfeffer's data, is given by the law of Gay-Lussac for gases. van't Hoff showed therefore that the perfect gas equation

$$PV = nRT \qquad \text{or} \qquad P = cRT$$

expressed the relation between osmotic pressure, concentration and temperature. The fact that R has the same numerical value in both equations shows the strict analogy between the two forces. A thermodynamic proof of this relation based on Henry's law will be given later when we discuss the thermodynamic considerations of solutions.

The more accurate measurements of Morse and Frazer, and Berkeley and Hartley showed, however, that these simple relationships may hold reasonably well at high dilution but no longer hold in the case of more concentrated solutions (above 0.2 molar). That this is the case is not at all surprising when we consider that many gases if subjected to pressures equal to the osmotic pressure of dilute solutions would deviate in their behavior from the gas laws on account of mutual attractions between their molecules. Later attempts, therefore, have been made to introduce corrections for these influences in the simple

[1] Pub. No. 198, Carnegie Institution of Washington.
[2] *Phil. Trans.*, **A**, 206, 486 (1906).
[3] Cf. p. 257.
[4] *Z. physik. Chem.*, **1**, 481 (1887).

equation given above. A discussion of these theories will be considered in a separate section. An interesting analogy between osmotic and gaseous pressures has been demonstrated by Ramsay,[1] who employed the apparatus shown in the accompanying diagram (Fig. 5). Palladium, at a temperature of 300° C., is permeable to hydrogen but does not allow nitrogen to pass through it and may, hence, be considered as a semi-permeable membrane with respect to a mixture of these gases. A mixture of these gases, rich in nitrogen, is introduced into the palladium bulb P which is attached at J to the glass tube M containing mercury which serves as a manometer to indicate the pressure of the gases in P. Let this pressure have an initial value p, which is the sum of the partial pressures of the hydrogen, p_{H_2}, and nitrogen, p_{N_2}. If we now enclose the bulb P in a gas-tight vessel through which we pass hydrogen under atmospheric pressure, the latter will pass through the palladium until the partial pressure of hydrogen on both sides of the membrane is equal to 1 atmosphere. The total pressure registered on the manometer at equilibrium will therefore be greater than p. The excess pressure within the bulb may be considered as the osmotic pressure of the solution of nitrogen in hydrogen when separated from pure hydrogen by a semi-permeable membrane permeable to the latter gas. Whether the osmotic pressure of solutions is similarly brought about by a condition of inequality in pressures due to a difference in concentration of the pure solvent on both sides of the membrane will be discussed more fully when the question of the mechanism of osmosis is considered.

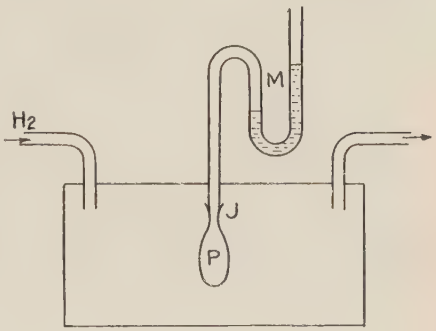


FIG. 5

The Determination of Molecular Weights in Solution: The most accurate determinations of the molecular weights of substances are based on two principles. They may either be determined in the gaseous state by the use of the principle of Avogadro, or in solution by the measurement of any of the colligative properties which we have considered. The experimental details of the latter method will be discussed in the next section and we shall, therefore, limit ourselves here to a consideration of the general applicability of the different methods and their mode of application. These relations all express some property of the solution, osmotic pressure, boiling point, etc., as a function of the concentration of the dissolved substance. If we express, then, these concentrations in terms of moles (i.e., in terms of the weight of substance dissolved, divided by its molecular weight), we have all the data necessary for computing the molecular weight of the substance in solution. Thus, by ex-

[1] W. Ramsay, *Phil. Mag.*, [5] **38**, 206 (1894). P. Villard, *Compt. rend.*, **126**, 1413 (1898). J. Duclaux, *J. Chim. Phys.*, **10**, 528 (1912).

pressing the formula for osmotic pressure by the equation

$$PV = \frac{m}{M}RT \qquad \text{or} \qquad M = \frac{RTm}{PV},$$

where m is the weight in grams of the substance dissolved in volume V, we can calculate the molecular weight, M, of the substance from the observed osmotic pressure, P. The difficulties involved in the experimental determination of osmotic pressures, however, have prevented its application to the determination of molecular weights except, possibly, in the case of colloids, where the methods of freezing and boiling points are very erroneous.

Molecular Weight Determinations from Vapor Pressure Lowerings: The determination of molecular weights by the lowering of the vapor pressure has been made possible by recent improvements in the mode of measurement of such lowerings. The following results obtained by Menzies [1] illustrate the possible accuracy attainable by such determinations.

TABLE II

VAPOR PRESSURE LOWERINGS OF SOLUTIONS OF NAPHTHALENE IN BENZENE (MENZIES)

Weight of Dissolved Substance in Grams	Volume of Solution in Cc.	Vapor Pressure Lowering	Molecular Weight Obtained
0.3115	48.1	60.1	128.6
0.5118	49.1	105.2	127.5
0.3237	46.1	65.2	128.0
0.5092	46.8	101.6	127.3

The results are seen to agree well with the theoretical value 128.0. The molecular weight is calculated in the above from the formula relating to osmotic and vapor pressures

$$p_0 - p = \frac{P\sigma}{\rho - \sigma},$$

in which p_0 is the vapor pressure of the pure solvent, p of the solution, P the osmotic pressure, ρ the density of the solution and σ the vapor density at pressure p. Assuming the applicability of van't Hoff's law, we can substitute for P its value as derived above and obtain the relation

$$p_0 - p = \frac{mM_0\,760}{M\,1000(\rho - \sigma)},$$

the pressures being expressed in mm. of mercury. In the equation m is the number of grams of solute dissolved in 1 liter of solution, M its unknown molecular weight and M_0 the molecular weight of the solvent in the form of

[1] *Z. physik. Chem.*, **76**, 231 (1911).

vapor. We thus are able to calculate M by substituting the observed values for the other symbols.

The determination of molecular weights from vapor pressure lowerings is especially useful where the freezing-point method is not applicable. Moreover, as it can be applied over a long range of temperature, it can be used to determine the change in molecular weight, as due to association, for example, with temperature.

Molecular Weights from Freezing and Boiling Points: Perhaps the most widely applied method of determining molecular weights in solution has been by means of freezing and boiling points. From the equations for these properties we can determine also the molecular complexity of the substance in solution by seeing what multiple of the commonly accepted molecular weight must be taken to obtain the same value for the constant in these equations as is obtained from the experimental value of the heat of fusion or vaporization. In this way interesting information has been obtained regarding the effect of various solvents on the association of dissolved substances. The solvents of the benzene series, for example, have been found to favor polymerization, whilst the analogues of formic acid tend towards the formation of simple molecules.

Since the present chapter is not intended to consider the case of solutions of electrolytes, mere mention can only be made of the fundamental importance of the study of the colligative properties in connection with the questions of electrolytic dissociation, as, for example, in the modern theories of activity.

Experimental Study of Dilute Solutions

Modern physical chemistry traces its origin from the epoch-making discoveries of van't Hoff, Arrhenius and others in the field of solutions. During the several decades that followed these discoveries the problem of solutions was the chief center of interest, and it is only in the past decade that its numerous offspring—colloidal chemistry, electro-chemistry, etc.—have usurped its former prominence. As in other fields, the early experimental studies merely aimed to corroborate and firmly establish the then existing theories and it is only in more recent times that a finesse of technique has been developed which is capable of defining the limits of applicability of the theoretical developments and offering grounds for their alteration and expansion. It is therefore important to have a knowledge of the more reliable experimental methods now available for the investigation of solutions. In the present section a brief description is given of the most refined experimental methods which have been developed for this purpose, together with such other similar measurements as seem of interest, and their applicability to the subject in question will be discussed.

Experimental Determination of Osmotic Pressure. Method of Pfeffer: The first quantitative measurements of osmotic pressure were made by the botanist Pfeffer [1] whose results formed the experimental basis for the theoretical reasoning of van't Hoff.

[1] Pfeffer, *Osmotische Untersuchungen*, Leipzig, 1877.

The apparatus used by Pfeffer (Fig. 7) consisted of a porous clay cell, z, containing the solution to be studied, to which was attached a manometer, m, for measuring the pressure developed when the cell was surrounded by pure water. The whole apparatus in position for use is shown in Fig. 6. Pfeffer prepared his cells in the following manner. The clay cell was treated first with a dilute solution of potassium hydroxide and then with a 3 per cent solution of nitric acid, after which it was carefully dried. The wall of the clay cell was then completely filled with water by repeated evacuation under an air pump whilst immersed in water. It was then allowed to stand for some hours in a 3 per cent solution of copper sulphate and filled with the same solution. The interior was then quickly rinsed out several times with distilled water and quickly dried as well as possible by wiping the interior with strips of filter paper. After the cell had stood in the air until the exterior was just moist to the touch, it was filled with a three per cent solution of potassium ferrocyanide and placed again in the copper sulphate solution. After standing thus for one to two days

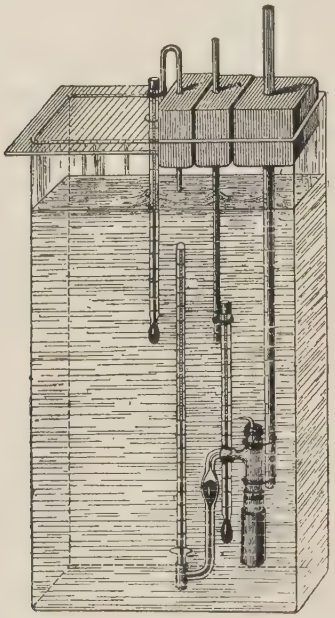


Fig. 6. Pfeffer's Apparatus for Osmotic Pressure Measurement

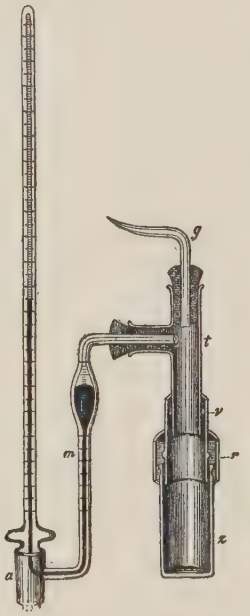


Fig. 7

it was closed and allowed to develop what pressure it would by reason of the difference in osmotic pressure between these two solutions. After another interval of from one to two days the cell was opened and filled with a solution containing 1.5 per cent potassium nitrate and 3 per cent copper ferrocyanide. Under these conditions a pressure of about three atmospheres is developed. If the cell was to be used for measuring pressures greater than three atmospheres, it was tested under a greater pressure, which is readily done by increasing the concentration of the potassium nitrate in the test solution. It was found desirable to have the initial pressure develop slowly and to allow the cell to be subjected for some time to this low pressure. This slow initial development of pressure seems to have the effect of pressing the membrane material into the cell wall in such a manner that its continuity is not destroyed. If the pressure is allowed to develop rapidly, the manometer shows a rapid initial rise to a maximum, but this pressure soon falls. In such cases, Pfeffer frequently noted that a brown

stain of copper ferrocyanide appeared on the exterior of the cell, showing that the membrane had been ruptured.

Remarkably good success was had by using the above method. Of twenty cells scarcely a failure was recorded, while before resorting to the expedient of partial drying no membrane was successfully deposited on the surface of the cell. For this reason Pfeffer had been compelled in his first investigations to use cells in which the membranes had been deposited at some distance beneath the surface of the cell wall. In order to deposit the membrane in such a position, the cell with its wall filled with water was placed in a 3 per cent copper sulphate solution for fifteen to twenty minutes and filled with a solution of potassium ferrocyanide of the same (3 per cent) concentration. When the membrane was formed in this way, by diffusion, it occupied a position near the inner surface of the cell.

Membranes deposited on the surface of a cell, by the method outlined above, not only have the advantage that they are immediately in contact with the solution under investigation, but they are also more easily and successfully formed than when the membrane is formed within the interior of the cell wall. In certain cases membranes could be readily formed on the surface of the cells while successful deposition in the cell wall was either impossible or could be accomplished only with the greatest difficulty, even though the cells in both cases were from the same source. It is interesting to note that Pfeffer found that cells made by only one manufacturer out of the ten whose products were tested gave satisfactory results and that he had at his complete disposal the entire use of a pottery for the solution of his difficulties.

Pfeffer undoubtedly had very reliable cells at his disposal as he found that 15 to 20 per cent solutions of dextrin showed absolutely no leakage of solute after a period of fourteen days, and a 5 per cent solution of sucrose after being kept in the cell twelve days at a temperature of 12°–20° showed no detectable amount of solute in the surrounding solvent. The idea of using $Cu_2Fe(CN)_6$ as a membrane was due to Traube,[1] who had previously shown it to be impermeable to certain dissolved crystalloids while permitting water to pass through it. Pfeffer also used membranes of other materials and carried out measurements with dilute solutions of sugar, dextrose, gum arabic, electrolytes, etc. Lack of accuracy in Pfeffer's results with such solutes as sucrose can hardly be traced to faulty membranes. From his results, he showed that osmotic pressure was proportional to concentration, was much smaller in the case of colloidal substances like gum arabic than with molecularly dispersed systems, and that osmotic pressure increased linearly with temperature.

Method of Morse and Frazer: The two chief problems which confront the investigator who attempts a direct measurement of osmotic pressure are the production of a membrane which is truly semi-permeable and an accurate determination of the pressure produced, with careful control of temperature and accurate analyses of the solutions. If any of these factors is disregarded, it is perfectly evident that no great reliability can be placed on the results. The details of the method of Pfeffer, as is evident from their description, fail in certain respects to provide the necessary refinements and, though the importance of Pfeffer's pioneer work cannot be overestimated, it required the development of innumerable, practically important details to give the method sufficient accuracy over a wide range of concentration to make it applicable to the theoretical problems of dilute solutions.

H. N. Morse, while engaged in the electrolysis of solutions of permanganates with porous diaphragms in order to prepare solutions of pure permanganic acid, noticed, on occasions, the osmotic activity of such cells in whose pores manganese dioxide had separated. This suggested the idea of depositing copper ferrocyanide membranes electrolytically in porous

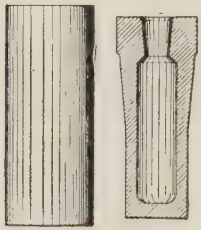
[1] M. Traube, *Zentral. f. mediz. Wiss.*, 1864; *Archiv. Anat. Wiss. Med.*, p. 87 (1867).

clay cells for the purpose of measuring osmotic pressure. The method was described by Morse and Horn [1] in 1901. While the easy formation of an osmotically active membrane by this method was readily obtained, there remained a very great number of experimental details the solution of which was necessary before quantitative measurements could be made. In fact all and more of the difficulties encountered by Pfeffer had to be solved.

Morse and Frazer,[2] therefore, undertook in 1901 an extensive improvement in the mode of measurement of osmotic pressure, utilizing the electrolytic method of Morse and Horn for depositing the membrane. As a result of the improvements in the details of measurement introduced by these investigators in collaboration with their students, the measurement of osmotic pressure has reached a high state of refinement and accuracy in the limited number of cases to which it is applicable. The limit of its applicability, however, has prevented its extended use, but this phase of the problem will be considered in detail later. We shall next describe the various parts of the apparatus which are used in actual measurements.

The Cells. By chance these investigators had at their disposal about 20 cells with which their first work was done. Unfortunately later experience showed these cells could not be duplicated by the potter. Various potteries were called on to assist in the production of satisfactory cells. In every case failure resulted. It was then evident the problem would have to be solved first in the laboratory. After trying various expedients, Frazer while associated with Morse developed a method of fabricating the cell that satisfied the requirements for certain solutes. Microscopic examination of sections of good and bad cells showed that fine, uniform texture was required. Fig. 8 *a* and *b* show sections of one of the potter's cells and one made in the laboratory, respectively.

The cross section of an ordinary porous cell as produced in the industry (Fig. 8 *a*) is seen to lack uniformity and contain numerous air blisters. Since the function of the cell in measurements of osmotic pressure is to secure a support for the semi-permeable membrane, it is perfectly obvious that the fineness of texture of the latter will depend on the pores of the cell itself. If there should happen to be a point where the cell wall is highly porous, the membrane, if deposited at all over this area, must necessarily be held but loosely, and the exertion of any pressure at this point would easily disrupt it. Hence the attainment of cells of uniform and fine texture is necessary.



Cylinder of Pressed Clay — Fashioned Cell

Fig. 9

The first step taken was to select two clays of such composition that it would be unnecessary to add any of the ground material used by the potter as a "binder." These were carefully treated to remove coarse particles after which the mixture was molded under pressure into cylindrical form, Fig. 9 *a*, and then the cell was turned on the lathe to the proper size and shape, Fig. 9 *b*, dried, and burned. The upper portion was then glazed to permit attachment of the manometer.

Such cells were entirely satisfactory for measurements with non-electrolytes of high molecular weights. To make them applicable to substances of small molecular weights, the porosity of the cells has recently been further decreased and a more perfect support given

[1] *Am. Chem. J.*, **26**, 80 (1901).

[2] *Am. Chem. J.*, **28**, 1 (1902); **29**, 173 (1903); **32**, 93 (1904); **34**, 1 (1905); **36**, 1 (1906); **37**, 324, 425, 558 (1907); **38**, 175 (1907); **39**, 667 (1908); **40**, 1, 194, 266, 325 (1908); **41**, 1, 92, 257 (1909); **45**, 91, 237, 383, 517, 554 (1911); **48**, 29 (1912); Publication Carnegie Inst. No. 198.

Fig. 8

Photo-micrographs of Porous Cells

the membrane by the precipitation "in situ" of an inert substance like $MgSiO_3$.[1]

A cross section of such a cell is shown in Fig. 8 *c*, the dark portion being the precipitated filling. Its opaqueness compared to the rest of the cell shows the fineness of its pores. Such cells are more efficient supporters of the membrane, allow only a minimal leakage, a rapid attainment of equilibrium, and require no period of "seasoning." Recent experiments, by the above-mentioned investigators, however, have shown that the presence of too fine and thick a cell may vitiate the results, due possibly to the interference of electrokinetic effects. The presence of a fine capillary system in the cell may bring about a condition of affairs in which the solution proximate to the semi-permeable membrane has a concentration (due to the capillary effect of the cell pores) far different from that of the solution and hence the results obtained, though reproducible and apparently referring to the solution studied, really refer to entirely different conditions.

The desideratum, therefore, is the production of a very fine material on the surface of which the membrane may be deposited and which will present its other surface to the pure solvent, thus obviating any concentration change due to capillary effects.

After its preparation and filling, the cell is boiled in water and all air bubbles removed by continued electrolysis of a 0.05 per cent Li_2SO_4 solution, the water transferred electro-endosmotically serving to remove the last traces of air. The cell, after electrolysis with distilled water to remove the last traces of electrolyte, is ready for the deposition of the semi-permeable membrane.

Recently the character of the cell wall of osmotic pressure cells has been improved in the following way:

The clay cell made as described above is immersed in vacuo in its liquid ethyl ester of ortho silicic acid. After the interstices have been filled by this ester the excess liquid is removed and the surface wiped dry with filter paper. The cell is then exposed in a closed vessel saturated with water vapor. The following reaction takes place in the pores of the cell

$$Si(OC_2H_5)_4 + 4H_2O = Si(OH)_4 + 4C_2H_5OH.^2$$

The result, in effect is to give a porous cell filled with pure silica gel on which the membrane of copper ferrocyanide is deposited preferably by the method of Pfeffer described above. Such cells are now being used for the study of solutions of substances which could not be studied with the best clay cells obtainable.

In preparing these "filled" cells the greatest danger comes from the fact that the cell wall is frequently ruptured by the strains set up in the wall when the ester dries out and contracts.

The Membrane. Despite efforts to find other membranes, the $Cu_2Fe(CN)_6$ first described by Traube has always been most satisfactory for osmotic pressure measurements, and has been exclusively used in these researches. The mode of deposition, however, and the care exercised in its development have been altered.

[1] Grollman and Frazer, *J. Am. Chem. Soc.*, 45, 1710 (1923).

[2] See Grimaux, *Compt. rend.*, 98, 1434 and 1485 (1884).

The mode of deposition of the membrane by the method of Morse and Horn is shown in the accompanying diagram (Fig. 10). The porous cup (*a*) in which the membrane is deposited is held by means of a rubber stopper (*b*) in a glass vessel (*c*) containing a 0.1 per cent solution of $K_4Fe(CN)_6$. The cell is filled with a 0.1 M solution of $CuSO_4$ and a current allowed to pass through the solutions from a copper anode (*d*) held in the porous cup by a rubber stopper. A platinum sheet which surrounds it serves as the cathode (*e*). The funnel (*f*) and exit tube (*g*) serve to renew the $K_4Fe(CN)_6$ solution so as to prevent an accumulation of alkali during the electrolysis.

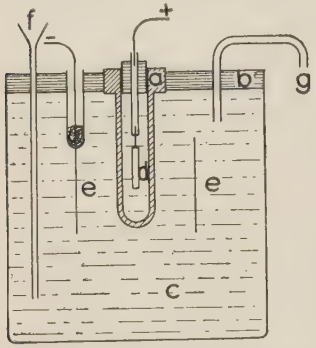


FIG. 10. Apparatus for Membrane Deposition

When the cell is put through the membrane-forming process for the first time, there is a temporary fall of resistance as the cell wall becomes filled with the electrolyte and a rapid rise thereafter as the membrane continues to form. A maximum resistance is soon reached, after which the process should be discontinued and the cell placed in water. After several days, the process is repeated, and, after several repetitions, a good cell will readily develop considerable pressure with a cane sugar solution. It is, however, still imperfect and for complete development may require as much as six months or a year of such treatment. Apparently worthless cells have proved useful with no other treatment than being left in distilled water which is frequently changed.

The Measurement of Pressure. The pressure developed may be determined by reading the volume of a column of nitrogen enclosed in a carefully calibrated manometer, by means of a cathetometer.

The upper end of the manometer (4, Fig. 11) consists of a thread of mercury, thus obviating the error of the unknown change in bore due to constriction in sealing the manometer end. The use of glass manometers suffers from the disadvantage that the time for the attainment of equilibrium is long; their accuracy decreases with increased concentration due to deviation of the gas from Boyle's law, occlusion of gas and increased percentage error of readings; and, finally, they are easily broken at high pressures or by temperature changes. Application has, therefore, been made of a resistance pressure gage [1] and of the water interferometer,[2] using the change in the index of refraction due to the pressure exerted in the experiment as a means of measuring this pressure. This apparatus has been further modified [3] to give an increased accuracy and ease of manipulation over the original apparatus. The more recent form is shown in Fig. 12.

This instrument has been described by Grollman and Frazer.[4] It has a range of 30 atmospheres. This can be increased by the use of thin glass plates inserted in the path of the beam passing through the non-pressure side.

Since the range of 30 atmospheres corresponds to 3000 divisions on the interferometer and since readings on the latter are capable of duplication within 10 divisions, the pressure readings are accurate to 0.1 of an atmosphere. The accuracy may be increased by the use of a liquid more compressible than water or by the use of a longer pressure chamber and wider windows. The length of the pressure chamber of the instrument used was 80 mm. By arranging the mirrors and prisms of the interferometer so that there is a greater distance between the two beams, larger windows can be used in the pressure gage, which insures more accurate readings.

[1] Frazer and Myrick, *J. Am. Chem. Soc.*, **38**, 1907 (1916).
[2] Frazer, Van Doren, Parker and Lotz, *J. Am. Chem. Soc.*, **43**, 2497 (1921).
[3] Grollman and Frazer, *J. Am. Chem. Soc.*, **45**, 1710 (1923).
[4] *J. Am. Chem. Soc.*, **45**, 1714, 1715 (1923).

The older methods of joining the manometer to the cell have been improved by Frazer and Myrick,[1] who devised the apparatus shown in Fig. 13.

"*M* (Fig. 13) is the clay cell with the membrane of copper ferrocyanide *K* deposited on its exterior. This extends only as far as indicated by the heavy line *K*, the neck and shoulder of the cell being glazed to ensure tight joints. *J* is the bronze cylinder into which the cell is fastened by means of the plug *P*. The latter has three legs upon which the apparatus stands and which serve as a means of screwing the plug into the cylinder. *N* is a

Fig. 11. Manometer

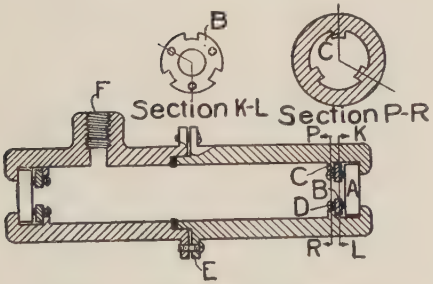


Fig. 12. Cross Section of Interferometer

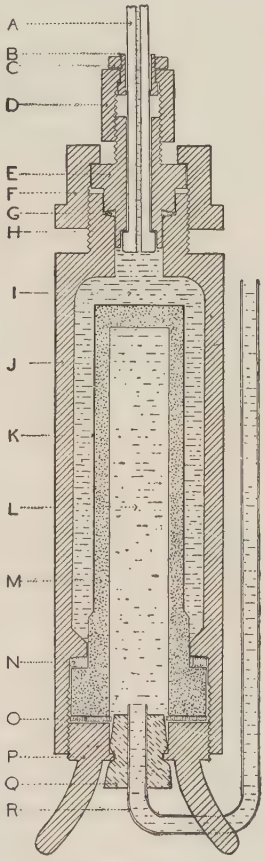


Fig. 13

thick rubber washer and *O* is a piece of commercial 'Rainbow Packing,' about a millimeter and a half thick. This packing gives perfect satisfaction, while the ordinary rubber will not withstand higher pressures. At all other joints *N*, *G*, *H*, the packing is surrounded on all sides so it can not flow; hence in these places the softer rubber washers answer very well. In fact, it is desirable to have *N* and *G* thick (about 4 mm.) and soft so that initial pressure may be secured by their compression.

"*R* is a glass U-tube held in the mouth of the cell by means of the rubber stopper *Q*.

[1] *J. Am. Chem. Soc.*, **38**, 1907 (1916).

This is simply to keep the solvent L up in the cell and yet leave it open to the atmosphere. I is the solution to be measured. E is the manometer attachment and is fastened onto the cylinder by means of the nut F, G being a thick rubber washer described above. A is a piece of capillary glass tubing to which the manometer is sealed. The square shoulder at the lower end of A is secured by sealing onto a piece of tubing, of the size desired for A, another piece, having somewhat larger external dimensions. The joint is kept soft and the glass allowed to flow together until a considerable enlargement is secured, the internal diameter being kept of original size by careful blowing. After cooling, the larger piece of tubing is cut off close to the enlarged joint. A is then mounted in the lathe and the enlarged end ground to the desired size and shape. In this manner the lower end of A is made to fit accurately into the lower end of E, as shown in the diagram. To hold A in position, B is sealed onto A by means of sealing wax (Khotinsky) and after putting D into position, C is screwed onto B It will be seen that by turning D to the left, A is raised and held tightly in position in E against the washer H. By turning D to the right, A is lowered and excess solution is allowed to escape. This method of joining glass and metal is of general application and has proven most satisfactory. Such a joint will hold tight under any pressure which will not actually break the glass."

In the use of the interferometer cell, a similar attachment is used with the exception that the tube A is of brass and the cell contents are separated from the interferometer cell by a mercury trap.

With the above-described apparatus and the great care in the details of carrying out experimental determinations, such as temperature control, analysis, etc., to which reference must be made to the original articles, data have been obtained over a range of temperatures from 0° to 80° and over the complete range of concentrations in the case of sucrose solutions, as well as measurements of mannite, phenol, etc. The results obtained for some of these substances are given in the following tables.

TABLE III[1]

OSMOTIC PRESSURES OF SUCROSE SOLUTIONS

Grams Sugar/1000 Cc. of Solution	Grams Sugar/1000 G. of Water	Equilibrium Time, Minutes	Osmotic Pressure, Atmospheres
		30°	
478.3	680	90	57.5
472.0	665	12	56.6
597.0	958	90	87.2
605.4	980	150	90.4
608.5	990	165	92.0
700.2	1260	195	129.5
695.0	1242	225	127.4
781.4	1549	180	169.1
781.4	1549	225	168.6
777.3	1533	90	164.1
831.5	1758	300	(198.2)
826.2	1737	195	200.2
839.8	1796	165	206.1

[1] Lotz and Frazer, *J. Am. Chem. Soc.*, **43**, 2504 (1921).

TABLE III. *Continued.*

55.7°

477.2	674	22	61.0
481.4	685	20	63.1
610.6	996	35	97.4
612.7	1000	16	98.7
702.3	1270	30	132.4
706.4	1284	55	133.5
782.5	1556	75	170.6
791.9	1590	90	178.7
856.5	1877	120	222.0
842.9	1810	135	213.8
900.2	2112	165	259.3
910.6	2190	135	256.6
No analysis.....	.....	135	273.0

Osmotic Pressure of Sucrose Solutions at 0°

(Morse, Frazer and Zies)

Concentration (Weight Normal Solutions)	Osmotic Pressure Observed	Ratio of Osmotic to Gas Pressure
.1	2.46	1.11
.2	4.72	1.06
.3	7.09	1.06
.4	9.44	1.06
.5	11.90	1.07
.6	14.38	1.08
.7	16.89	1.08
.8	19.48	1.09
.9	22.19	1.10
1.0	24.83	1.12

TABLE IV[1]

Osmotic Pressure of Aqueous Phenol Solutions at 30°

O.p. calc. from				O.p. calc. from			
Concn.	Formula $P=\frac{RT}{V_0}\left(x+\frac{x^2}{2}+\frac{x^3}{3}+\cdots\right)$	O.p. obs.	$\frac{\text{Calc. o.p.}}{\text{Obs. o.p.}}=$ degree of assoc.	Concn.	Formula $P=\frac{RT}{V_0}\left(x+\frac{x^2}{2}+\frac{x^3}{3}+\cdots\right)$	O.p. obs.	$\frac{\text{Calc. o.p.}}{\text{Obs. o.p.}}=$ degree of assoc.
0.1	2.46	1.46	1.68	0.6	14.73	7.62	1.93
.2	4.92	2.84	1.73	.7	17.16	8.82	1.95
.3	7.38	3.93	1.88	.8	19.59	10.05	1.95
.4	9.83	5.12	1.92	.9	22.02	11.28	1.95
.5	12.28	6.40	1.92	—	—	—	—

[1] Grollman and Frazer, *J. Am. Chem. Soc.*, **45**, 1707 (1923).

The Method of Berkeley and Hartley: [1] The method of these investigators differs from those hitherto described in that instead of measuring the pressure that is exerted due to diffusion of the solvent into the solution, this diffusion is prevented by the application of a pressure to the solution just sufficient to prevent passage of solvent into the solution.

A cross section of the apparatus is represented in Fig. 14.

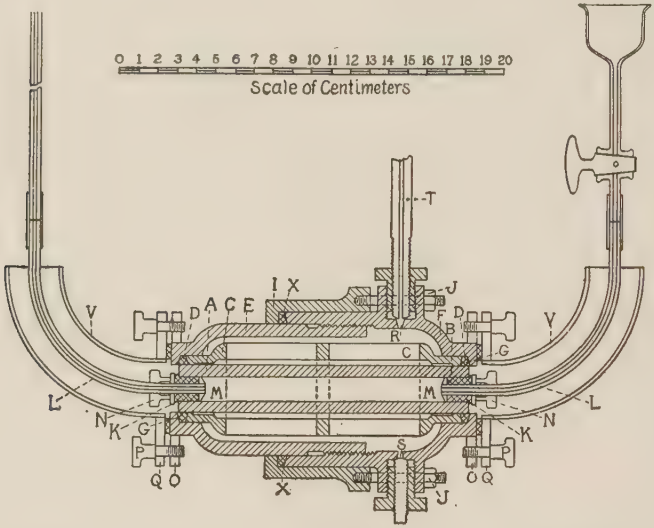


FIG. 14. Apparatus of the Earl of Berkeley and E. G. J. Hartley

"*AB* is a porcelain tube 15 cm. long, 2 cm. external and 1.2 cm. internal diameter, the ends of which are glazed. This tube carries the semi-permeable membrane as close to the outer surface as possible. *CC* is a gun-metal cage against the ends of which the dermatine rings *DD* are compressed when the two parts *E* and *F* of the outer gun-metal vessel are screwed together. The ends of this cage have shallow radial grooves cut out of them so as to prevent the dermatine rings from rotating and rubbing the membrane during the operation of screwing *E* and *F* home. The length of the cage is such that, when finally set up, the dermatine rings just overlap the ends of the porcelain tube.

"The outer gun-metal vessel (capacity about 250 cc.) contains the solution which, when a pressure is applied to it, forces the dermatine rings against the bevelled faces *GG*, and thus causes a tight joint to be made with the porcelain tube. The joint between *E* and *F* is made good by another dermatine ring *X*, which is compressed between the metal ring *I* and the nuts *JJ*.

"The ends of *AB* are closed by pieces of thick-walled rubber tubing *KK*, through which the brass tubes *LL* are passed; a water tight joint between *LL* and the inside of the porcelain tube is obtained by compressing the rubber between the metal washers *MM* and the nuts *NN*. The brass tubes are joined by rubber tubing, one to a glass tap and the other to an open glass capillary—the latter, which we shall call the water gauge, was graduated in millimeters and calibrated; one centimeter of the bore contains 0.00312 cc. The outer ends of *E* at *F* have threads cut on them to receive the brass rings *OO*, which in their turn are per-

[1] *Phil. Trans.*, **A 206**, 486 (1906).

forated by screw-holes to receive the thumbscrews *PP*, by means of which, together with a rubber washer, a tight joint is made between the flanges *QQ* of the curved metal tubes *VV* and the ends of *E* and *F*.

"The perforation *R* is for filling the apparatus with solution, and also for connecting to the pressure apparatus, while *S* serves to empty the vessel."

A determination is made by filling the porcelain tube containing the membrane with water, which partially fills the attached capillary tube, surrounding it with the solution to be investigated, and gradually applying a pressure which could be regulated and measured, until there was no flow of water from the interior of the solution. This pressure was determined by observing the rates of movement of the water meniscus in the capillary tubes at pressures near the osmotic pressure. A correction to this reading was applied, due to leakage resulting from imperfect contact between the dermatine rings and the membrane, or from cracks in the glaze. Measurements by the above method are fairly rapid, inasmuch as it is not necessary to wait for equilibrium to set in by a diffusion through the cell, which diffusion is usually slow near the equilibrium pressure.

The same investigators [1] have devised a dynamic method which is based on the measurement of the rate of flow of solvent into the solution which gives results concordant with other methods, if we consider the initial flow only and assume it to be that which would occur if the water were caused to pass through the membrane by the application of a mechanical pressure equal to the osmotic pressure.

Vegard,[2] who has described a simple form of the above apparatus, showed that the rate of flow gradually diminishes and, hence, the initial rate of flow alone gives accurate results. The relation between the velocity of osmotic flow and osmotic pressure has been further investigated by Sebor [3] and Antropoff [4] and is illustrated in the following table (V) by some results from the work of Berkeley and Hartley.[5]

TABLE V

Relation between Velocity of Osmotic Flow and Osmotic Pressure

Pressure in Atmospheres	Diffusion Velocity in Mm. of Capillary per Second	Ratio of Diffusion Rates	Ratio of Pressures
20.41	0.1075	1	1
40.82	0.2203	2.05	2
61.24	0.3240	3.01	3
81.65	0.4303	4.00	4
102.06	0.5319	4.95	5
122.47	0.6378	5.93	6

Numerous other experimental measurements of osmotic pressure have been

[1] *Proc. Roy. Soc.*, **A 82**, 271 (1909).
[2] *Phil. Mag.*, [6] **16**, 247, 396 (1908); *Proc. Camb. Phil. Soc.*, **15**, 13 (1909).
[3] *Z. Elektrochem.*, **10**, 347 (1904).
[4] *Z. physik. Chem.*, **76**, 721 (1911).
[5] *Proc. Roy. Soc.*, **A 82**, 273 (1909).

made by E. Cohen and J. W. Crommelin,[1] A. Ladenburg,[2] R. H. Adie,[3] G. Tammann,[4] A. Naccari,[5] A. Ponsot,[6] P. S. Barlow,[7] S. Kahlenberg,[8] G. Flusin,[9] W. G. Wilcox,[10] E. Fouard,[11] C. F. Nelson,[12] and A. E. Koenig.[13] Due to the lack of sufficient perfection in the apparatus used by these investigators, however, their results are conflicting and will, therefore, not be further discussed here.

Some of the results of Berkeley and Hartley are given in Table VI which also contains the results obtained by Frazer and Myrick for comparison.

TABLE VI

Osmotic Pressure of Sucrose Solutions

Grams of Sucrose in 1000 Cc. of Solution	Grams of Sucrose per 1000 Grams of Water	Osmotic Pressure		
		Berkeley and Hartley		Frazer and Myrick
		P at 0° (Observed)	P at 30° (Calculated)	P at 30° (Observed)
180.1	202	13.95	15.48	15.59
300.2	370	26.77	29.72	29.78
420.3	569	43.97	48.81	47.88
540.4	820	67.51	74.94	73.06
660.5	1133	100.78	111.87	109.10
750.6	1430	133.74	148.46	148.80

A new method of measuring osmotic pressure has been described recently [14] to which the student is referred for details.

"The ordinary method for measuring osmotic pressure and the only one which has so far given satisfactory results consists in the use of a porous clay cell, which acts as a support for a copper ferrocyanide membrane. The solution is placed on one side of the cell, a suitable manometer attached and the equilibrium pressure determined when pure solvent is placed in contact with the other side of the membrane. The method has been refined so as to give

[1] *Z. physik. Chem.*, **64**, 1 (1908).
[2] *Ber.*, **22**, 1225 (1889).
[3] *J. Chem. Soc.*, **59**, 344 (1891).
[4] *Z. physik. Chem.*, **9**, 97 (1892).
[5] *Atti. accad. Lincei*, **6**, 32 (1897); *Nuov. cim.*, [4] **5**, 141 (1897).
[6] *Compt. rend.*, **125**, 867 (1897); **128**, 1447 (1899).
[7] *Phil. Mag.*, [6] **10**, 1 (1905); [6] **11**, 595 (1906).
[8] *J. Phys. Chem.*, **10**, 141 (1906); **13**, 93 (1909).
[9] *Ann. chim. phys.*, [8] **13**, 480 (1908).
[10] *J. Phys. Chem.*, **14**, 576 (1910).
[11] *Compt. rend.*, **153**, 769 (1911); *J. phys.*, [5] **1**, 627 (1911); **2**, 269 (1912); *Bull. soc. chim.*, [4] **11**, 249 (1912).
[12] *J. Am. Chem. Soc.*, **35**, 658 (1913).
[13] *J. Phys. Chem.*, **22**, 461 (1918).
[14] R. V. Townnend, *J. Am. Chem. Soc.*, **50**, 2958 (1928). Also W. C. Eichelberger, Dissertation, Johns Hopkins Univ., 1930.

reliable results with solutes of high molecular weight but up to the present it has not been applicable to solutions of electrolytes, on account of the difficulty in obtaining suitable membranes which would be impermeable to the ions.

" The present method makes use of two general properties of liquids: first, that changing the pressure on a liquid surface changes its vapor pressure, and, secondly, that liquids possess an internal pressure or cohesion force so that (in the absence of excess dissolved gases) it is possible to place a tension on the two ends of a column of liquid.[1]

Outline of the Method

" In the method to be described here, the solution to be measured—for example a salt solution—is placed in contact with its vapor. Some of the pure solvent is also placed in contact with the vapor. Since the vapor pressure of the solution is less than the vapor pressure of the pure solvent at the same temperature, in the case mentioned, water vapor will distil from the pure solvent into the solution. It is seen that the vapor phase may be regarded as a perfect semi-permeable membrane permitting the passage of the molecules of solvent only.

" In order to permit the measurement of the osmotic pressure the liquid water is located within the capillaries of a thin porous plate. The capillaries are of sufficient size to permit the liquid water to pass readily to the surface of the plate, but so small that the maximum capillary rise is somewhat greater than the maximum osmotic pressure to be measured. Below the plate is a quantity of liquid water and below this a column of mercury. The weight of the water and mercury places a tension on the water at the surface of the plate. At equilibrium this force (corrected for any difference in heights between the water and solution) equals the osmotic pressure of the solution. The equilibrium point is determined by measuring the rates of distillation from the plate to the solution under different tensions. These rates are plotted against the corresponding tensions. The osmotic pressure, which corresponds to the tension at zero distillation, is obtained from the curve by extrapolating to zero."

Measurement of Relative Osmotic Pressures: A number of methods have been devised which, though incapable of giving any absolute values, nevertheless furnish us with useful information regarding the relative values of the osmotic pressures of different substances. The cells of plants and animals consist of protoplasm enclosed in walls which, being strong and resistant, maintain their shape and size when immersed in solutions of other substances. These walls are permeable to water and aqueous solutions but are also lined on the inside with a thin membrane which is semi-permeable, allowing only water to pass through it, but no dissolved substances. The Dutch botanist De Vries[2] first applied such cells to the determination of osmotic pressures, using cells from the plants—*Tradescantia discolor*, *Curcuma rubicaulis* and *Begonia manicuta*—which he found most suitable for such work.

Fig. 15*a* shows the normal appearance of such cells as seen under the microscope. If now the cell is surrounded by a solution having the same osmotic pressure as the cell contents, it will maintain its normal appearance and the same is true if it is surrounded by a solution of smaller osmotic pressure in which case any distension of the semi-permeable membrane is prevented by the resistant cell wall. If, however, the cell is surrounded by a solution of greater osmotic pressure than its own, water will leave the cell and cause its contents to shrink, giving the appearance of Fig. 15*b*. By determining the lowest concentrations of various substances which are necessary to prevent this

[1] See also Washburn, *J. Am. Ceram. Soc.*, **1**, 29 (1918).

[2] *Z. physik. Chem.*, **2**, 415 (1888); **3**, 103 (1889).

contraction of the semi-permeable membrane, we have the relative concentrations necessary to produce the same osmotic pressure. The reciprocals of these isosmotic or isotonic concentrations, when expressed in molar quantities, are known as isotonic coefficients and show the relative osmotic pressures of solutions of equal molecular concentration. Some of De Vries' results are given below (Table VII).

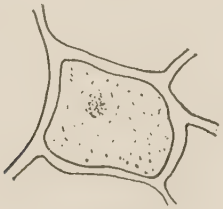


FIG. 15*a*

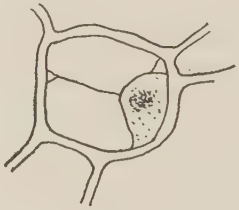


FIG. 15*b*

TABLE VII

ISOTONIC COEFFICIENTS OF AQUEOUS SOLUTIONS (DE VRIES)

Substance	Isotonic Coeff.
Glycerol	1.78
Cane Sugar	1.88
KNO_3	3.00
NaCl	3.05
$CaCl_2$	4.33
$MgCl_2$	4.33

These values were of great use in the development of early theories of solution, clearly showing the effect of dissociation of electrolytes on the colligative properties of solutions.

Hamburger[1] has employed red blood corpuscles for the same purpose. The lowest concentrations of various substances necessary to cause the corpuscles of defibrinated deer's blood to settle, leaving a liquid above, have the same osmotic pressure. The results obtained by this method,[2] as well as those obtained in the study of the effect of various substances on the movement of various bacteria,[3] all yield results which agree within the limits of error of the experimental determinations.

The method of Tammann[4] consists in noting the optical results due to diffusion through a semi-permeable membrane of an inorganic material such as $Cu_2Fe(CN)_6$. The slight currents due to diffusion through the membrane are observed by a refractometer and their absence is used to indicate the presence of an isotonic solution.

[1] *Z. physik. Chem.*, **6**, 319 (1890).

[2] W. Löb, *Z. physik. Chem.*, **14**, 424 (1894). H. Köppe, *Z. physik. Chem.*, **16**, 261 (1895). S. G. Hedin, *Z. physik. Chem.*, **21**, 272 (1896).

[3] Wladimiroff, *Z. physik. Chem.*, **7**, 529 (1891).

[4] *Wied. Ann.*, **34**, 299 (1888).

Recently [1] efforts have been made to measure the osmotic pressure of acetone solutions by using sheets of rubber as the semipermeable membrane. The membrane was found to be imperfectly semipermeable, but the author concludes from his experiments that had it been truly semipermeable the results would have agreed with those predicted by the gas laws.

The Experimental Determination of Vapor Pressure: Of the various experimental studies of the colligative properties, none is more desirable than that of vapor pressure. Of all the colligative properties, vapor pressure and osmotic pressure determinations alone may be made at various temperatures. The fact that, from the values for the former, we may derive the values of the other colligative properties makes this experimental study most desirable. The chief problems are constant temperature regulation, purity of reagents, the removal of all dissolved gases, and a sensitive instrument for pressure mensuration. The experimental methods of measuring vapor pressures are divisible into two types, the static and dynamic. The static method was first applied by von Babo,[2] whose work, together with that of Wüllner,[3] led to the first generalizations on the relation between vapor pressure lowering and concentration. These workers showed that the lowering of the vapor pressure is proportional to the concentration of solute; that, for the same solution, the lowering due to a non-volatile substance is, at all temperatures, the same fraction of the vapor pressure of the pure solvent.

The later methods of Tammann [4] and Raoult,[5] though allowing only a limited degree of accuracy, nevertheless led Raoult, as a result of his exhaustive experimental investigations, to the enunciation of his law already discussed. The method of Raoult consisted in introducing a pure liquid into a barometer tube inverted over mercury, a solution with the same liquid as solvent into another similar tube, and then comparing the heights of the mercury column in these tubes with that of a third which was connected to a volume of air of known pressure, all three being connected through a common reservoir to an adjustable mercury container. By use of his simple apparatus Raoult could determine a difference in pressure of 10 mm. of Hg with an accuracy of 2 per cent.

Dieterici [6] first used a differential method for the determination of vapor pressure lowering. This method depending as it does on a direct measurement of the difference in pressures between solvent and solution, instead of absolute measurements of both, is capable of most refined accuracy and all recent methods are based on this principle. Dieterici used the movement of a glass plate (0.08 mm. thick) as measured by its torque effect on a quartz thread which was attached to a mirror as a means of measuring the difference in

[1] M. J. Murray, *J. Phys. Chem.*, **33**, 896 (1929).

[2] L. v. Babo, Über die Spannkraft des Wasserdampfes in Salzlösungen, Freiburg (1847).

[3] *Ann. Physik*, [2] **103**, 529 (1858); **105**, 85 (1858); **110**, 564 (1860).

[4] *Ann. Physik*, [3] **24**, 523 (1885); **36**, 692 (1889).

[5] *Compt. rend.*, **103**, 1125 (1886); **104**, 976, 1430 (1887); **107**, 442 (1888); *Z. physik. Chem.*, **2**, 353, 372 (1888); *Ann. chim. phys.*, [6] **15**, 297 (1888); **20**, 375 (1890).

[6] *Ann. Physik*, [3] **50**, 47 (1893); **62**, 616 (1897); **67**, 859 (1899).

pressures between solvent and solution. Readings could be made with an accuracy of 0.001 mm. Hg over a range of 0.1 to 0.01 mm. His apparatus is shown in Fig. 16. The method of Dieterici was further improved by Maier [1] and Seiferheld.[2] Improvements in the construction of a differential manometer were carried out by Lord Rayleigh,[3] Hering [4] and Mündel.[5] Applying the Rayleigh manometer to the measurement of vapor pressure lowerings, Frazer and Lovelace [6] have described a method of precision which has yielded quite accurate data for solutions of mannite, sucrose, KCl, NaCl, LiCl and HCl over a range of from 20°–30°.[7]

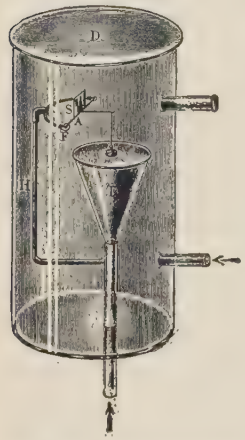


FIG. 16. Apparatus of Dieterici

The following description of the apparatus is taken from the original paper of Frazer and Lovelace. The apparatus is shown in Figs. 17, 18 and 19.

"The entire apparatus is built around the Rayleigh manometer, shown in Fig. 17. One side of the manometer communicates with the solvent bulb *H* and the other with the solution bulb *I*. 1, 2, 3, 4, 5, 6 (Fig. 19) are mercury traps which serve as stopcocks. They may be opened or closed by adjusting the position of the mercury reservoirs. The long ones are of barometer height, while the short ones are about 100 mm. high. Since ordinary stop-cocks are not employed, the use of lubricant is avoided. The large bulb, *C*, is introduced to increase the capacity of the system and thus facilitate removal of air from solution and solvent. *B* is a phosphorus pentoxide bulb provided with a ground glass joint and mercury seal. *A* is the McLeod gage. All connecting tubes are seven mm. internal diameter.

"After the apparatus was put together all parts of it except the Rayleigh manometer and the phosphorus pentoxide bulb were thoroughly steamed out.

"The bulbs containing solution and solvent are immersed in a water bath, the temperature of which does not vary over periods of several hours more than 0.001°, as read on a Beckmann thermometer. Experience has shown that the Rayleigh manometer is quite sensitive to fluctuations of 0.003° in the bath temperature, if these fluctuations occur over short intervals of time. While it is thus necessary to avoid sensible variations in the temperature of the solution and solvent, no such constancy of temperature is necessary for the other parts of the system.

"In carrying out a complete experiment the following procedure is adopted: The proper amount of carefully cleaned mercury is poured into each of the reservoirs attached to the open ends *M*, *M*, *M* of the apparatus and the entire system exhausted repeatedly to the

[1] *Ann. Physik*, [4] **31**, 423 (1906).

[2] Diss. Tübingen, 1911.

[3] *Z. physik. Chem.*, **37**, 713 (1901); *Trans. Roy. Soc.*, **196**, 205 (1901).

[4] *Ann. Physik*, [4] **21**, 319 (1906).

[5] *Z. physik. Chem.*, **85**, 435 (1913).

[5] *J. Am. Chem. Soc.*, **36**, 2439 (1914); *Z. physik. Chem.*, **89**, 155 (1914).

[7] Frazer, Lovelace and Miller, *J. Am. Chem. Soc.*, **38**, 515 (1916); Frazer, Lovelace and Rogers, *ibid.*, **42**, 1793 (1920); Frazer, Lovelace and Sease, *ibid.*, **43**, 102 (1921); Frazer, Lovelace and Bahlke, *ibid.*, **45**, 2930 (1923); H. Parker, Dissertation, Johns Hopkins Univ. (1921); L. C. Beard, Dissertation, Johns Hopkins Univ. (1922); W. Norris, Dissertation, Johns Hopkins Univ. (1922); R. K. Taylor, Dissertation, Johns Hopkins Univ. (1923); S. S. Negus, Dissertation, Johns Hopkins Univ. (1923); Grollman, unpublished results (1924).

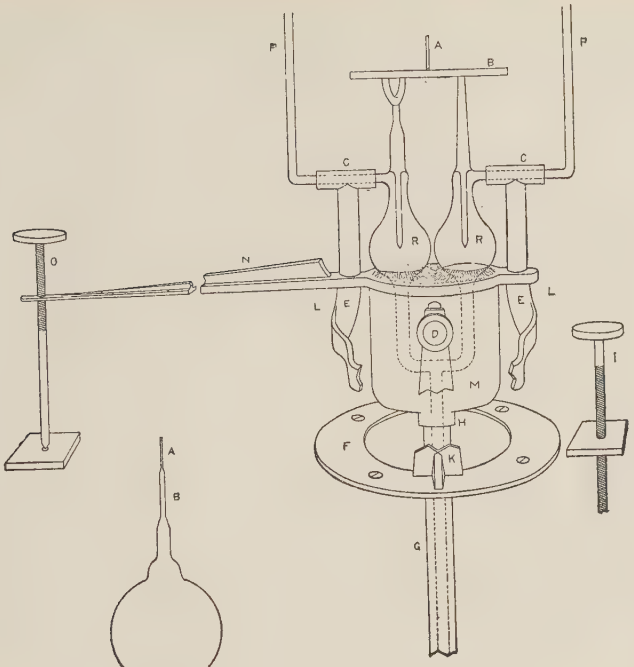


FIG. 18

FIG. 17

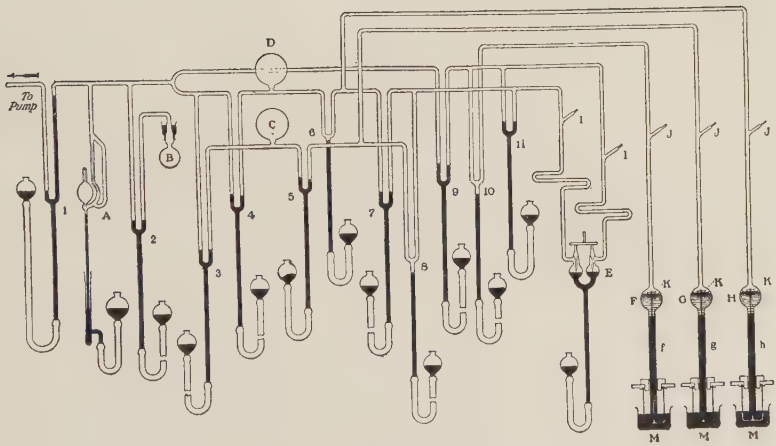


FIG. 19

highest vacuum attainable by the pump. The zero point is then determined, after which, solvent, partially freed from air by boiling, is introduced and the remaining trace of dissolved air removed, as described later. The solution, also partially freed from air, is next introduced, and, after complete removal of dissolved air, the zero point may be redetermined. Finally, the pressure of vapor over the solution is balanced against that of the vapor over the solvent and the scale deflection read. The entire apparatus having been exhausted, trap 5 is closed and the solvent, freed from air as completely as possible by long boiling, is introduced into the bulb. In this operation, the solvent need not come in contact with air and it is, therefore, possible to introduce into the apparatus solvent that is practically air-free. There is, however, in actual practice, always a trace of air to be removed after the solvent is in the bulb. This is accomplished in the following manner: Traps 1, 2 and 4 (Fig. 19) and the McLeod gage are closed, and trap 5 opened and allowed to stay open 24 hours. Trap 5 is then closed and 2 opened. After the absorption of water vapor by the phosphorus pentoxide in B is complete, the McLeod gage is opened and the pressure determined. The residual air is pumped out and the process repeated as many times as may be necessary for complete removal of dissolved air. The solvent, having once been freed from air, may remain in the apparatus indefinitely and it is possible at any time to examine its vapor for air. Trap 3 is now closed and 5 opened.

TABLE VIII

VAPOR PRESSURE LOWERING OF AQUEOUS MANNITE SOLUTIONS

Grams of Mannite per 1000 G. of Water (in Vacuo)	Conc. in Moles per 1000 G. of Solvent	$p_0 - p_1$ = Vapor Pressure Lowering in Mm. Mercury	Lowering Calc. According to Raoult's Law	Difference between Calc. and Obs. Lowerings
17.930	0.0984	0.0307	0.0311	0.0004
36.004	0.1977	0.0614	0.0622	0.0008
53.951	0.2962	0.0922	0.0931	0.0009
71.917	0.3945	0.1227	0.1239	0.0012
89.938	0.4938	0.1536	0.1547	0.0011
108.243	0.5944	0.1860	0.1858	− 0.0002
108.498	0.5958	0.1863	0.1862	− 0.0001
126.283	0.6934	0.2162	0.2164	− 0.0002
144.357	0.7927	0.2478	0.2469	− 0.0009
162.332	0.8913	0.2791	0.2772	− 0.0019
162.485	0.8922	0.2792	0.2775	− 0.0017
180.451	0.9908	0.3096	0.3076	− 0.0020

"Fig. 18 shows a device employed for partial removal of air from the solution before it is introduced into the apparatus. The bulb is drawn down at each end to a capillary and enough solution introduced, at the ordinary temperature, to fill the bulb completely at 85°–90°. The lower capillary is then sealed off, the upper end drawn down to a very fine capillary, A (about 0.05 mm.), and the whole heated to the temperature at which the solution completely fills the bulb and capillary. The latter is then sealed off and the solution allowed to cool and stand 24 hours in the partial vacuum thus obtained. The tip of the capillary is next broken off and the process repeated. Five repetitions of this operation are sufficient to remove nearly all the air. The solution is then introduced into the bulb I without coming in contact with the air and the last traces of dissolved air removed in the manner already described for the solvent. The extent to which the solution is concentrated during the process of removal of air after introduction into the bulb I may be accurately calculated and never exceeds 0.1 per cent. After the removal of air is complete, trap 4 is closed and 6 opened, and a measurement may now be taken.

"Observations on the Rayleigh manometer during the progress of the removal of air from the solution are very interesting. It is to be remembered that at this stage the vapor pressure of the air-free solvent is balanced against the pressure over the solution, which is equal to the vapor pressure of the solution plus a small air pressure. As long as any air remains in the solution (even the smallest trace), a very long time is necessary for the establishment of equilibrium after the opening of trap 6. The pressure in the solution limb of the manometer, at first very nearly the true vapor pressure of the solution, slowly increases for 24 or 48 hours, depending on how much air remains. After equilibrium is attained, the difference in pressure in the two limbs is read in the usual way by noting the scale deflection. To this apparent depression is added the air pressure in the system, subsequently determined by means of the McLeod gage, after absorption of the water vapor by the phosphorus pentoxide. The depression thus obtained agrees very closely, to about 0.001 mm., with the true depression measured later, after complete removal of air."

Results for mannite solutions, obtained by Frazer, Lovelace and Rogers,[1] are given in Table VIII.

Another form of differential manometer due to Smits[2] has found application in the accurate measurement of vapor pressure lowerings and is shown in Fig. 20. The lower narrow part of the manometer is filled with aniline (*A*) over which is a layer of water (*B*) which continues into the wider upper portion. This in turn is covered with a layer of oil to prevent any influence of the water vapor. For the mathematical theory of the readings the reader is referred to the original article of Smits or to Jellinek.[3]

Dynamic Methods: The dynamic methods of determining vapor pressure lowering are much simpler to carry out experimentally and hence have found wide application, though the results obtained lack somewhat the precision of the best static methods. One can, for example, determine the pressure at which a pure solvent and its solution boil at the same temperature as had been done by A. A. Noyes and C. G. Abbott,[4] H. M. Goodwin and G. K. Burgess,[5] and A. W. C. Menzies.[6] The method of Walker[7] consists in passing a known volume of air through the pure solvent and the solution; by determining the amount of vapor so removed, we can calculate the vapor pressure of the solution in question.

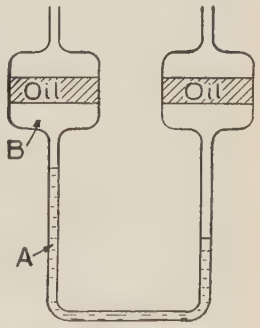


FIG. 20. Manometer of Smits

Excellent results have been obtained by the Earl of Berkeley, E. G. J. Hartley and C. V. Burton,[8] who improved the method by passing the current of air over the liquids in order to avoid change of pressure in the apparatus. These investigators determined the amount of vapor lost by the bulbs containing the solution, while Washburn and Heuse[9] weighed the amount of vapor

[1] *J. Am. Chem. Soc.*, **42**, 1801 (1920).
[2] *Z. physik. Chem.*, **39**, 386 (1906).
[3] Lehrbuch der Physikalischen Chemie, vol. 2, p. 759 (Stuttgart, 1915).
[4] *Z. physik. Chem.*, **23**, 56 (1897).
[5] *Z. physik. Chem.*, **28**, 99 (1899).
[6] *Z. physik. Chem.*, **76**, 231 (1912).
[7] *Z. physik. Chem.*, **2**, 602 (1888).
[8] *Phil. Trans. Roy. Soc.*, **A 209**, 177 (1909); **A 218**, 295 (1919).
[9] *J. Am. Chem. Soc.*, **37**, 309 (1919).

taken up by absorption in a suitable apparatus. The chief errors in the method are due to the difficulty in accurately measuring the aspirated air and maintaining constant temperatures.[1]

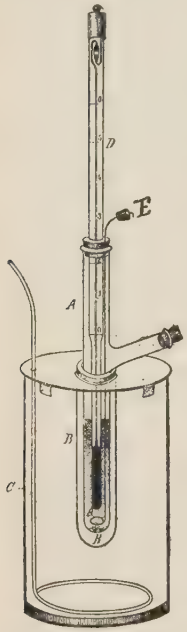


FIG. 21. Beckmann's Apparatus for Freezing-Point Determinations

The Experimental Determination of Freezing and Boiling Points: Of all the colligative properties, none lend themselves to experimental determination so easily as freezing and boiling points. The ease and accuracy with which thermometric readings may be made, especially differential readings, as by the Beckmann and platinum resistance thermometers, have made the wide application of such determinations possible. Moreover, since simple relationships are known, whereby the other colligative properties, such as osmotic and vapor pressures, may be calculated, these measurements are used where experimental difficulties make the direct determination of the others difficult or inaccurate. The great limitation in the value of freezing- and boiling-point data, however, lies in the fact that they are limited to a single temperature, and, hence, cannot, without doubtful assumptions, be applied over a range of temperatures.

The earliest determinations of freezing-point lowerings were made by Blagden,[2] who showed the proportionality between freezing-point lowering and concentration. Numerous experiments were later made by Rüdorff [3] and Coppet,[4] the former of whom developed experimental mechanical details and showed that, from many solutions, the solvent crystallized out in a pure form at the freezing point.

The extensive work of Raoult [5] led him to his generalization which we have already discussed. Other workers may also be mentioned, Hollemann,[6] Auwers,[7] Fabinyi,[8] Eykmann,[9] Klobukow,[10] but it was not until the work of Beckmann [11] that any experimentally accurate apparatus was devised.

His apparatus, which, due to its simplicity and accuracy, has found wide application, is shown in the accompanying diagram (Fig. 21).

[1] For some very recent determinations of vapor pressure lowerings see Bousfield, *Proc. Roy. Soc.*, **103A**, 429 (1923), and Dieterici, *Ann. Physik*, **70**, 617 (1923).

[2] *Phil. Trans.*, **78**, 277 (1788); Ostwald's Klassiker, No. 56, Leipzig (1894).

[3] *Ann. Physik*, [2] **114**, 63 (1861); **116**, 55 (1862); **122**, 337 (1864); **145**, 599 (1872).

[4] *Ann. chim. phys.*, [4] **23**, 366 (1871); **25**, 502 (1872); **26**, 98 (1872).

[5] *Ann. chim. phys.*, [5] **20**, 217 (1880); **28**, 133 (1883); [6] **2**, 66, 93 (1884); **4**, 401 (1885); **8**, 289, 317 (1886); *Jour. Phys.*, [2] **3**, 16 (1884); **5**, 65 (1886); *Z. physik. Chem.*, **9**, 343 (1892); Cryoscopie, Serie physico-mathematique, No. 13, Paris (1911).

[6] *Ber.*, **21**, 860 (1888).

[7] *Ber.*, **21**, 701 (1888).

[8] *Z. physik. Chem.*, **4**, 964 (1889).

[9] *Z. physik. Chem.*, **4**, 497 (1889).

[10] *Z. physik. Chem.*, **4**, 10 (1889).

[11] *Z. physik. Chem.*, **2**, 638 (1888).

Various refinements in experimental technique have been introduced by the numerous workers who have carried out freezing-point determinations. We may mention the work of Loomis,[1] Raoult,[2] H. C. Jones,[3] Wildermann,[4] P. B. Lewis,[5] Abegg,[6] Hausrath,[7] Ponsot,[8] Roloff,[9] and Richards.[10]

Due to the fact that the formation of a new phase at the freezing point is more regular in its action than at the boiling point, determinations of the former can be carried out with greater accuracy. In both determinations, however, the usual thermometric errors, such as irregularity in bore and sticking of the mercury thread, must be carefully considered and obviated. A source of considerable error is the variable depression of the ice point due to changes in volume of the bulb resulting from molecular changes in the glass with change of temperature. This error is obviated by keeping the thermometer at the temperature of the experiment for a long period and redetermining the ice point after the experiment. In this way its variability may be reduced to 0.0003° C.[11] In the case of precise measurements correction must also be made for pressure variations, both external and internal, which affect the readings. Nernst [12] first showed that in cryoscopic determinations constancy of temperature did not necessarily denote the freezing point, but that a final constant reading might result as well from a balance in the interchange of heat between the freezing mixture and the solution, and the establishment of equilibrium between the liquid and solid phases. Unless this convergence temperature coincides with the true freezing point, errors as high as 20 per cent in the value of the molecular depression could be introduced. Nernst and Abegg indicated, however, how the observed values could be corrected to give the true freezing point. The determination of the concentration at the freezing point is also of fundamental importance and numerous devices have been introduced to make this determination precise.

Of the more recent determinations of freezing points, we may mention the work of Beckmann,[13] Jahn,[14] Bedford,[15] Flügel,[16] Adams,[17] Cernatescu,[18] to which,

[1] *Ann. Physik*, [3] **51**, 506 (1894); **57**, 514 (1896); *Z. physik. Chem.*, **32**, 581 (1900); **37**, 408 (1901).

[2] *Z. physik. Chem.*, **27**, 622 (1898); *Ann. chim. phys.*, [7] **16**, 168 (1899).

[3] *Z. physik. Chem.*, **11**, 111, 529 (1893); **12**, 623 (1893); Carnegie Inst. Pub., No. 80, No. 180.

[4] *Z. physik. Chem.*, **15**, 337 (1894); **30**, 510 (1899).

[5] *Z. physik. Chem.*, **15**, 365 (1894).

[6] *Z. physik. Chem.*, **20**, 208 (1896).

[7] *Ann. Physik*, [4] **9**, 542 (1902).

[8] *Ann. chim. phys.*, [7] **10**, 79 (1897).

[9] *Z. physik. Chem.*, **7**, 323 (1891); **22**, 616 (1897).

[10] *Z. physik. Chem.*, **18**, 572 (1895); *J. Am. Chem. Soc.*, **25**, 291 (1903).

[11] Cf. Ostwald, Luther, Drucker, Physico-Chemische Messungen.

[12] Nernst and Abegg, *Z. physik. Chem.*, **15**, 681 (1894). Nernst and Hausrath, *Ann. Physik*, [4] **17**, 1018 (1905).

[13] *Z. physik. Chem.*, **44**, 169 (1903).

[14] *Z. physik. Chem.*, **50**, 129 (1904); **51**, 31 (1907).

[15] *Proc. Roy. Soc.*, **A 83**, 454 (1910).

[16] *Z. physik. Chem.*, **79**, 537 (1912).

[17] *J. Am. Chem. Soc.*, **37**, 481 (1915).

[18] *Ann. Sci. Univ. Jassey*, **10**, 259 (1920).

as well as to the work already cited, reference should be made for a description of the various details necessary for precise determinations. In the method of Adams, whose apparatus is shown in Fig. 22, a rapid and certain equilibrium is brought about by stirring with a large amount of ice; the depression of the freezing point is accurately determined by means of a thermocouple and sensitive potentiometer; and the analysis of the solution is made with a high degree of accuracy by the use of an optical apparatus.

Results obtained by Adams with aqueous mannite solutions are given in Table IX.[1]

TABLE IX

FREEZING-POINT DEPRESSIONS OF AQUEOUS MANNITE SOLUTIONS

Concentration Millimols per 1000 Grams H_2O	Freezing-Point Depression ($\Delta\tau$) in Degrees (Observed)	Calculated	Diff. Obs.-Calc. (10^{-4} Degrees)
4.02	.0074	.0075	0
8.42	.0157	.0156	1
14.04	.0260	.0261	− 1
28.29	.0525	.0525	0
62.59	.1162	.1162	0

Boiling-Point Determinations: The earliest measurements of the raising of the boiling point, due to the addition of a non-volatile solute to a solvent, were made by Faraday,[2] Griffiths,[3] and Legrand,[4] but no accurate work was done until the important work of Raoult [5] and Beckmann.[6]

Modifications of the Beckmann apparatus have been made which have rendered it a most precise method for physico-chemical measurements.[7] The boiling-point method has certain inherent errors which require special precautions unnecessary in the determination of freezing points. Care must be taken to measure the temperature of the solution rather than that of the vapor, which soon cools to its condensation point, giving the temperature of the boiling solvent. This error has been overcome by an ingenious device due to

[1] *J. Am. Chem. Soc.*, **37**, 492 (1915).

[2] *Ann. chim. phys.*, [2] **20**, 324 (1820).

[3] *Ann. Physik*, [2] **2**, 227 (1824).

[4] *Ann. chim. phys.*, [2] **59**, 425 (1835).

[5] *Compt. rend.*, **87**, 167 (1871); **122**, 1175 (1896); *J. Phys.*, [2] **8**, 1 (1889); *Ann. chim. phys.*, [6] **20**, 361 (1890); Tonométrie in Scientia (Carré et Naud, Paris, 1900).

[6] *Z. physik. Chem.*, **3**, 603 (1889); **4**, 532 (1889); **5**, 76 (1890); **6**, 437 (1890); **8**, 223 (1891); **15**, 656 (1894); **17**, 106 (1895); **18**, 473 (1895); **21**, 245 (1896); **22**, 609 (1896); **40**, 129 (1902); **44**, 161 (1903); **51**, 329 (1905); **53**, 137 (1905); **58**, 543 (1907); **63**, 177 (1908); **64**, 506 (1908); **78**, 725 (1912); **79**, 565 (1912); **86**, 337 (1914); **88**, 13, 23, 419 (1914).

[7] A. Smits, *Z. physik. Chem.*, **33**, 39 (1900); **39**, 404 (1902). Stahler's Handbuch der Arbeitsmethoden in Anorg. Chem., vol. III, pp. 131–164, Leipzig, 1913.

Cottrell [1] who, instead of immersing the thermometer bulb in the liquid, thereby running the risk of error due to superheating, places it in the vapor phase as in the case of a pure liquid, and causes the boiling liquid to pump itself over the thermometer bulb. The apparatus of Cottrell is shown in Fig. 23. The tube *d* serves as a pump and insures the passage of solution in intimate contact with its vapor over the thermometer bulb. The glass sheath, *J*, which is attached to the ground glass stopper, serves to protect the bulb from the condensed vapor. The solute is introduced through the tube *H* and the sample for analysis removed by the application of air pressure at its open end.

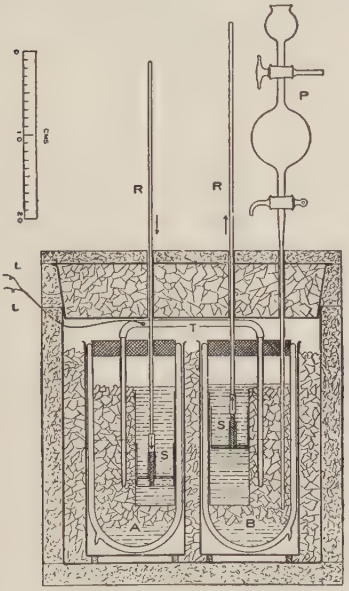


FIG. 22. Freezing-Point Apparatus of Adams

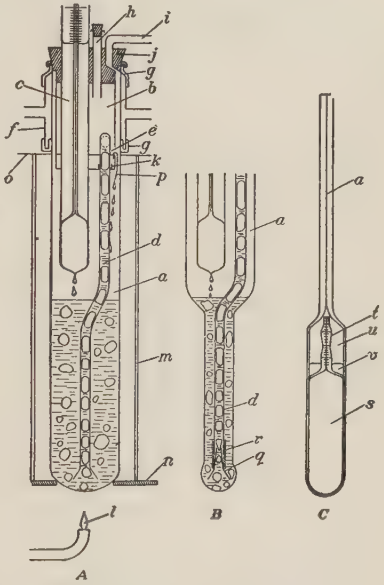


FIG. 23. Boiling-Point Apparatus of Cottrell

The method of heating the solution to be studied is also of primary importance. The early methods in which the heat was applied externally have been replaced by electrical devices first introduced by Bigelow.[2] This method, further improved by Beckmann [3] and Mathews,[4] consists in heating the solution by an electric current which passes through a platinum spiral placed in the solution. The use of this method may be limited by electrolysis which may occur in the solution. Inasmuch as the boiling point is greatly influenced by pressure changes, it is not only necessary to maintain a constant external pressure, by the use of a suitable manostat, but the difference in boiling point

[1] *J. Am. Chem. Soc.*, **41**, 721 (1919).
[2] *Am. Chem. J.*, **19**, 581 (1897).
[3] *Z. physik. Chem.*, **63**, 187 (1908); **78**, 725 (1912); **88**, 23 (1914).
[4] *Trans. Am. Electrochem. Soc.*, **19**, 81 (1911).

of the various layers of the liquid due to hydrostatic pressure of the liquid above it must also be considered. In order to eliminate the influence of the temperature of the environment on that of the liquid under investigation, Beckmann has introduced an apparatus which is surrounded by a mantle in which the pure solvent is maintained at its boiling temperature.

For a description of the various forms of apparatus in use, the reader is referred to the original papers of the numerous investigators, especially the comprehensive work of Beckmann and the authors already cited.[1]

In the method of Sakurai, superheating of the boiling liquid is prevented by passing the vapor of the pure solvent through the pure liquid solution. The vapor condenses in the liquid, which is previously heated almost to its boiling point, the heat thus liberated raising the temperature to its boiling point.

Thermodynamic Considerations of the Laws of Dilute Solutions

In our previous considerations we have developed the laws of dilute solutions with special reference to the ultimate particles or molecules which make them up. As in other branches of theoretical chemistry, this point of view, despite the many advantages which it offers, is not essential, but we may develop all our generalizations by thermodynamic considerations, that is, by considering the energy relations involved in the various equilibria with which we have to deal. The study of solutions from the thermodynamic standpoint was first developed by van't Hoff, who was led to their study by his epochal work on the energy relations of chemical reactions and chemical equilibrium.[2] The essential results of van't Hoff's theories have also been developed, without reference to the concept of osmotic pressure, by Planck,[3] who is to be considered, with van't Hoff, as the co-founder of the modern theory of solutions. The general thermodynamic theory has also been expanded chiefly by van der Waals,[4] Van Laar,[5] J. W. Gibbs,[6] G. N. Lewis,[7] and E. W. Washburn.[8]

van't Hoff's Proof of the Identity of the Gas and Osmotic Pressure Formulæ: As we have already mentioned (pp. 353 and 358), thermodynamic considerations

[1] See also Sakurai, *J. Chem. Soc.*, **61**, 989 (1892); Landsberger, *Ber.*, **31**, 461 (1898); Walker and Lumsden, *J. Chem. Soc.*, **73**, 502 (1898); Speyers, *J. Phys. Chem.*, **1**, 766 (1898); Rose-Innes, *J. Chem. Soc.*, **81**, 682 (1902); Burt, *J. Chem. Soc.*, **85**, 339 (1904); Turner, *J. Chem. Soc.*, **97**, 1104 (1910); Drucker, *Z. physik. Chem.*, **74**, 612 (1912); Washburn and Read, *J. Am. Chem. Soc.*, **41**, 734 (1919); Reihenberg and Brauer, *Z. physik. Chem.*, **95**, 184, 512 (1920); Menzies and Wright, *J. Am. Chem. Soc.*, **43**, 2314 (1921); Spencer, *J. Am. Chem. Soc.*, **43**, 301 (1921).

[2] *Z. physik. Chem.*, **1**, 481 (1887).

[3] *Ann. Physik*, [3] **32**, 462 (1887). *Z. physik. Chem.*, **1**, 577 (1887); **2**, 405 (1888); **6**, 187 (1890). *Ann. Physik*, [4] **10**, 436 (1903).

[4] *Z. physik. Chem.*, **5**, 133 (1890).

[5] *Z. physik. Chem.*, **15**, 457 (1899); Sechs Vorträge über das thermodynamische Potential (Vieweg u. Sohn, Braunschweig, 1906).

[6] *Nature*, **55**, 461 (1897).

[7] *J. Am. Chem. Soc.*, **30**, 668 (1908). Thermodynamics, by Lewis and Randall, McGraw-Hill & Co., N. Y., 1923.

[8] *J. Am. Chem. Soc.*, **32**, 657 (1910).

alone do not allow the development of all the relations of solutions but we must start with some empirical relationship whose accuracy we assume. The identity of the equation $PV = nRT$ for both gaseous and osmotic pressures was first shown by van't Hoff. The following demonstration follows more closely that given by Rayleigh.[1] In this derivation the applicability of Henry's law will be assumed. This law, which states that the concentration of a gas dissolved in a liquid is proportional to the pressure of the gas at that temperature, has been shown to hold in those cases in which the solute has the same molecular form in the gaseous and dissolved states, and the assumption of its validity may, therefore, be considered as permissible in normal cases.

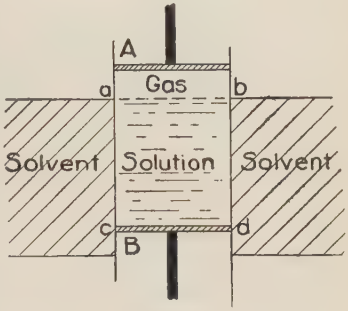


FIG. 24

Let us consider a reversible cyclic process carried out at a constant temperature, T, in which one mole of a dissolved gas is removed from a solution and then restored to its original condition, by use of the imaginary device shown in Fig. 24. A gas, whose pressure is p, in equilibrium with its solution, of osmotic pressure P, is separated from the latter by a semi-permeable membrane ab which only permits the gas to pass through it. Let us assume the vapor pressure of the solvent to be negligible compared with that of the gas. The walls of the cylinder, ac and bd, in which the solution is contained, are permeable to the solvent but do not allow the gas to pass through. The ends of the cylinder are closed by impermeable pistons A and B. Consider the following reversible process:

(1) Let the pistons A and B move upward so that a volume v, equal to the volume occupied by 1 gram-mol. of the gas at pressure p, is transferred through the membrane ab from the solution to the gas. The piston A therefore moves upward through a volume v, while the lower piston B moves through a volume V, equal to the volume of solution in which 1 gram mol. of the gas is dissolved. The solvent corresponding to this volume of solution simultaneously passes through the walls ac and bd. The maximum work done by the system in the reversible movement of the upper piston is pv while that done upon the system by the external surroundings in moving the lower piston is $-PV$, the negative sign indicating work done on the system. Hence the net work done in this stage is $pv - PV$.

(2) We wish now to restore one gram-mol. of the gas at a pressure p to the solution by a reversible and isothermal path so as to obtain the maximum work. Consider a volume v of the gas at pressure p, separated from the system. Let this gas expand isothermally and reversibly to practically infinite volume, so that the maximum work done in this process is

$$\int_{v_0}^{v_\infty} p\,dv = \int_{v_0}^{v_\infty} \frac{RT}{v}\,dv = RT\int_{v_0}^{v_\infty} \frac{dv}{v} = RT\ln\frac{v_\infty}{v_0}.$$

[1] *Nature*, 55, 253 (1897).

If the gas is now brought into contact with a volume V of solvent, it will dissolve infinitely slowly, since it is infinitely dilute, and the process will, therefore, be reversible. If the gas is gradually compressed by a frictionless piston, it will dissolve and the work done on the system by this process will be

$$-\int_{v_0}^{v_\infty} p_1 dv_1.$$

To evaluate this integral we must obtain a relation between p_1 and v_1. They are not related by the equation $p_1 v_1 = RT$ since at any stage of the solution process we no longer are dealing with one mole, some of the gas having already dissolved. When one mole of the gas has dissolved, the pressure of the piston is p so that, if we assume the validity of Henry's law regarding the proportionality being the amount of gas dissolved and its pressure, $\frac{p_1}{p}$ mole of gas will dissolve at the pressure p_1, leaving $1 - \frac{p_1}{p}$ undissolved. Applying the perfect gas equation to this amount of gas, we have at any stage

$$p_1 v_1 = \left(1 - \frac{p_1}{p}\right) RT,$$

and substituting for p its value, $\frac{RT}{v}$, we finally obtain

$$p_1 = \frac{RT}{v + v_1}$$

as our desired relation with which we may now derive the value of the integral

$$-\int_{v_0}^{v_\infty} p_1 dv_1 = -\int_{v_0}^{v_\infty} RT \frac{dv_1}{v_1 + v} = -RT ln \frac{v_\infty + v}{v}.$$

Since v is negligible compared to v_∞, we can write the last expression as

$$-RT ln \frac{v_\infty}{v}.$$

If now we return this volume of solution to the original solution, which process involves no work, we have our original system and hence the sum of the work terms done in this reversible and isothermal cycle must be equal to zero. That is,

$$pv - PV + RT ln \frac{v_\infty}{v} - RT ln \frac{v_\infty}{v} = 0$$

or

$$pv = PV.$$

But, by the perfect gas law, $pv = RT$. Hence, also,

$$PV = RT,$$

which is our desired relationship.

Relation between Osmotic Pressure and Vapor Pressure Lowering of a Solution: The vapor space above a solution which contains but one volatile constituent may be regarded as an ideal semi-permeable membrane permitting the removal of this constituent only. Let us imagine an apparatus as in Fig. 25, which consists of a cylinder fitted above with a piston which permits the passage of only the vapor of the solvent and at the bottom with a membrane which permits the passage of only the liquid solvent. Intervening between the solution and piston is a gas (helium, for example) which dissolves but slightly in the liquid and serves to transmit the pressure exerted by the piston. If a pressure p is put on the system by the piston which is equal to the osmotic pressure P of the solution, then equilibrium must exist at both the upper and lower membranes, otherwise a continuous circulation of the solvent would occur through the cell. Therefore, the partial pressure of the solvent in the gas space beneath the upper piston must be equal to the vapor pressure of the pure solvent outside and the osmotic pressure may be defined as the excess pressure which must be put on a solution in order to make the vapor pressure from the solution equal to that of the pure solvent at the same temperature. The effect of mechanical pressure on the vapor pressure of a liquid was first shown by Thomson and is expressed in the following equation:

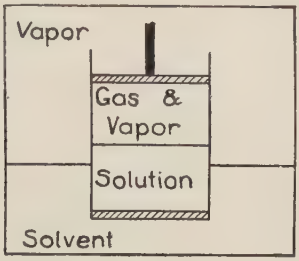


FIG. 25

$$\frac{dp_0}{dP} = \frac{V_0}{v},$$

where P is the applied pressure, V_0 is the molal volume of the liquid and v its molal volume in the vapor state.

For the relation between osmotic pressure and vapor pressure at equilibrium, we have from the above relation

$$\frac{dp}{dP} = -\frac{V_0}{v}.$$

Here, V_0 is the molal volume of the solvent in the solution. Then, since

$$v = \frac{RT}{p},$$

$$dP = -\frac{RT}{V_0} \cdot \frac{dp}{p}.$$

But since

$$\frac{dp}{p} = -\frac{dx}{1-x},$$

$$dP = \frac{RT}{V_0}\frac{dx}{1-x},$$

the integral of which gives

$$P = \frac{RT}{V_0}[-ln(1-x)],$$

which on expansion becomes

$$P = \frac{RT}{V_0}(x + \tfrac{1}{2}x^2 + \tfrac{1}{3}x^3 + \cdots).^1$$

In the case of dilute solutions, where x is small, the above equation reduces to $PV_0 = xRT$. The same relation may be shown in the following manner:

The osmotic pressure of a solution is only a manifestation of the lack of equilibrium between solution and pure solvent which also manifests itself in the vapor phase by a difference in vapor pressure of the two. By the following isothermal and reversible cycle we wish to derive a relation between the osmotic pressure and lowering of the vapor pressure due to the presence of a non-volatile solute. Let us imagine a cylinder, as shown in the accompanying diagram (Fig. 26), containing a solution in contact with its vapor at a pressure p. The cylinder is closed at the bottom by a piston ab acting as a semipermeable membrane by means of which the pure solvent can be removed osmotically from the solution. Let p_0 be the vapor pressure of the pure solvent and P the osmotic pressure of the solution.

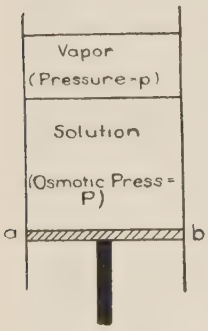


Fig. 26

(1) By means of the piston ab, which, acting as a semi-permeable membrane, allows the passage of solvent but is impermeable to the solute, let us remove osmotically and reversibly the volume of solvent dv. The work done by this process is $-Pdv$, the negative sign indicating work done on the system. (2) Let us allow this amount of solvent to be distilled isothermally and reversibly and expanded to yield its vapor at a pressure, p. By this reversible expansion at the temperature T, we gain an amount of work for one mole equal to

$$RTln\frac{p_0}{p}.$$

If the amount contained in the volume dv was dx moles, the work done by the system will be

$$dxRTln\frac{p_0}{p}.$$

(3) If this vapor is now condensed at the temperature T and pressure p, in contact with the solution, the heat expended by the condensation will be equal to that gained by the system in the evaporation considered in (2) and hence these two effects cancel one another and need not be evaluated.

[1] See Findlay, Osmotic Pressure, page 61.

Our system has now returned to its original state, and since the cyclic process has been carried out isothermally and reversibly, the net work must be zero, that is,

$$-Pdv + dxRTln\frac{p_0}{p} = 0.$$

If M is the molecular weight of the solvent in the vapor state, $\frac{Mdx}{dv}$ will be the density of the liquid solvent which we shall denote by ρ. Substituting in the above equation for $\frac{dx}{dv}$ its value $\frac{\rho}{M}$, we obtain

$$ln\frac{p_0}{p} = \frac{PM}{\rho RT},$$

which is the required relation between the osmotic pressure of a solution, P, and the lowering of the vapor pressure of the pure solvent $p_0 - p$. The relation between vapor pressure lowering and osmotic pressure, as well as the variation of vapor pressure with hydrostatic pressure, has also been developed by J. J. Thomson [1] to which the reader is referred.

Raoult's Equation for Vapor Pressure Lowering: In the case of a dilute solution to which van't Hoff's law of osmotic pressure applies,

$$P = cRT,$$

where c is the molar concentration of the solution. We may therefore write

$$ln\frac{p_0}{p} = \frac{cM}{\rho}$$

or

$$ln\frac{p_0}{p} \propto c,$$

which is the thermodynamically accurate form of Raoult's law. If the solution is very dilute, i.e., $p_0 - p$ is very small, we may write

$$ln\frac{p_0}{p} = ln\left(1 + \frac{p_0 - p}{p}\right)$$

and, since the logarithm of one plus a very small number equals the number (McLaurin's theorem), we may write $\frac{p_0 - p}{p_0}$ for $ln\frac{p_0}{p}$. The term $\frac{M}{\rho}$ in the above equation is equal to V_0, the volume of one mole of the solvent which in a dilute solution can be set equal to V_1, the volume of one mole of the solution. Let us also write c as $\frac{N}{V}$, where N is the number of moles of solute contained in the volume V of solution. Substituting these values in the original equation, we obtain

[1] Applications of Dynamics to Physics and Chemistry.

$$\frac{p_0 - p}{p_0} = \frac{NV_0}{V} = \frac{N}{N_0},$$

where N_0 is the number of moles of solvent in which N moles of solute are dissolved. This is the simple equation of Raoult which we have already derived in a previous section on purely kinetic grounds.

Osmotic Pressure Formula for Higher Concentrations: The simple form of the van't Hoff equation $P = cRT$, though applicable to very dilute solutions, is, nevertheless, only a limiting form of a more general equation which we will now derive from the above relationship between osmotic and vapor pressures:

$$ln\frac{p_0}{p} = \frac{PM}{\rho RT}.$$

If V_0 is the molal volume of the solvent, we may substitute it for $\frac{M}{\rho}$ in the above equation and write it

$$P = \frac{RT}{V_0} ln\frac{p_0}{p},$$

which is an exact expression even at large concentrations, provided the perfect gas laws apply to the vapor and the effect of pressure on the molal volume V_0 be negligible. If we wish to express osmotic pressure in terms of the concentration of the solute, we must apply Raoult's law, i.e., substitute for $\frac{p_0}{p}$ its value obtained from the relation

$$p = p_0(1 - x),$$

where x is the molar fraction of the solute. Our equation then becomes

$$P = \frac{RT}{V_0} ln\left(\frac{1}{1 - x}\right) = \frac{RT}{V_0}[- ln(1 - x)].$$

On expanding the term $ln(1 - x)$, the last equation becomes

$$P = \frac{RT}{V_0}(x + \tfrac{1}{2}x^2 + \tfrac{1}{3}x^3 \cdots),^1$$

which is the accurate form of the equation required. In the case of very dilute solutions, x is very small and hence its higher powers may be neglected, so that the above equation may be written

$$PV_0 = xRT.$$

In the case of a solution in which 1 mole of solute is contained in a volume V of solution, this may be written $PV = RT$, which is the simple form of the van't Hoff equation.

[1] Cf. Findlay, Osmotic Pressure, Longmans Green & Co., 1919.

Bancroft and Davis [1] have recently derived two expressions

$$PV_m = RTln\left(\frac{p_0}{p_1}\right) \tag{1}$$

and

$$PV_1 = RT\left(\frac{N}{n}\right)ln\left(\frac{p_0}{p_1}\right), \tag{2}$$

in which P is the osmotic pressure of the solution p_0 and p_1 the vapor pressure of the solvent and solution; V_m is the gram molecular volume of the solvent in solution (assuming the mol. wt. is that in the vapor phase); V_1 is the volume in the solution of the mass of solvent containing 1 mol. of solute; N and n refer to solvent and solute respectively. The student is referred to the original article and also to the discussion [2] of these by Hildebrand.

Relation between Osmotic Pressure and Boiling-Point Elevation: A relation similar to those derived above will now be derived for the osmotic pressure and boiling-point elevation of a solution. Let us assume (Fig. 27) that we have a solution enclosed by means of a frictionless semi-permeable membrane *ab*, which acts as a piston, allowing solvent to be removed osmotically and reversibly. The solution, whose osmotic pressure is P, is at the temperature T, the boiling point of the pure solvent. Let dT be the boiling point elevation.

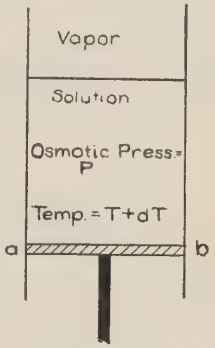


FIG. 27

(1) By means of the piston *ab* remove isothermally and reversibly a volume dv, whose weight is dx grams, of the solvent, whereby the work $-Pdv$ is involved. Since the process is isothermal an amount of heat, Q_0, equivalent to the work done on the system will be liberated.

(2) Allow this volume of solvent at temperature T to be evaporated isothermally, thus requiring an amount of heat equal to Ldx, where L is the latent heat of evaporation per gram of solvent at its boiling-point.

(3) The vapor and the solution are now heated to the temperature $T+dT$.

(4) At this temperature place the vapor in contact with the solution again, allowing it to condense and thereby giving an amount of heat L_1dx, where L_1 is the latent heat at the temperature $T + dT$.

(5) Lower the temperature of the system adiabatically to the original temperature T. The work in this process is very nearly equal and opposite in sign to the work in (3) and hence neither need be evaluated.

In this cycle work is done upon the system, heat is absorbed at T, and a larger amount is liberated at $T + dT$. Applying the first and second laws of thermodynamics to this cycle

[1] *Z. physik. Chem.*, **130**, 626 (1927); *J. Phys. Chem.*, **32**, 1 (1928).
[2] *J. Phys. Chem.*, **32**, 1086 (1928).

$$W = Q_1 - Q = L_1 dx - (Ldx - Q_0) = Pdv$$

and

$$(Q_1 - Q)/Q_1 = (T_1 - T)/T_1$$

where Q_1 is the net heat evolved at the higher temperature T_1 and Q that absorbed at the lower temperature T. So, on substituting, the latter expression becomes

$$Pdv = (dTL_1 dx)/(T + dT)$$

and writing $dx/dv = \rho$, the density of the solvent, we obtain

$$P = (L_1 \rho dT)/T_1,$$

where T_1 is the boiling point of the solution, which is our required relationship between the osmotic pressure, P, and the boiling-point elevation dT.

Since the solution is dilute, we can substitute for P its value in the equation $P = cRT$, where T is the boiling-point of the pure solvent. By making the assumptions that $T = T_1$ and $L = L_1$, which are approximately true for dilute solutions, we obtain

$$dT = \frac{RT^2 c}{L\rho}$$

which is the form for the relation between boiling point rise and concentration.

Osmotic Pressure and Freezing-Point Lowering: By considering a similar cyclical process in which an amount of solvent is removed from a solution at the freezing point of the pure solvent, T_0, allowed to freeze, cooling the solid and solvent to the freezing point of the solution $T_0 - dT$ returning the solid solvent previously removed back to the solution, by allowing it to melt, and finally restoring the whole system adiabatically to its original temperature, T_0, we can derive a similar relation between the freezing-point lowering and osmotic pressure of a solution, viz.:

$$P = (L_1 \rho dT)/T_1,$$

where L_1 is the latent heat of fusion per gram of solvent at T_1, the freezing-point of the solution, ρ its density, P the osmotic pressure and dT the freezing-point lowering. By a substitution for the value of P, as was made in the case of the boiling-point relationship, and by making similar assumptions, we obtain the equation connecting the freezing-point and concentration of a solution

$$dT = (RT_0^2 c)/L\rho,$$

where c is the concentration of the solute.

Kinetic Theories of Osmotic Pressure

As we have already seen (page 392), van't Hoff[1] first showed the analogy between osmotic and gas pressure by showing the applicability of the same equation

[1] *Z. physik. Chem.*, **1**, 481 (1887).

$$PV = RT$$

for both cases. In this equation, P is the osmotic pressure, when 1 mole of solute is contained in volume V of solution and is also the gas pressure that would be produced if this same amount of solute were present as a gas in the volume V. Just as the applicability of the perfect gas equation has been extended by the introduction of various correction factors, so numerous modifications of the simple osmotic pressure formula have been suggested which claim better concordance with experimental results and applicability over a wider range of concentrations. These relationships, being based on a kinetic conception of osmotic pressure, are usually referred to as kinetic theories of osmotic pressure.

It was found in the early work [1] on direct measurements of osmotic pressure that results more concordant with experiment are obtained if instead of expressing V in terms of the volume of solution we express it in terms of the volume of solvent (water) at its maximum density. This variation really amounts to correcting for the volume occupied by the dissolved substance, analogously to the correction made in the case of gaseous pressures for the volume occupied by the molecules themselves. A comparison of values obtained by these two methods is given in Table X.

TABLE X

Osmotic Pressure of Aqueous Sucrose Solutions at 20° from Measurements of Morse and Frazer

Weight Normal Concentration (Moles Sugar per 1000 Grams of Water)	Volume Normal Concentration (Moles Sugar per Liter of Solution)	Osmotic Pressure Calculated According to		Osmotic Pressure Observed
		Morse and Frazer	van't Hoff	
0.1	0.098	2.40	2.36	2.59
0.2	0.192	4.81	4.63	5.06
0.3	0.282	7.21	6.80	7.61
0.4	0.370	9.62	8.90	10.14
0.5	0.453	12.00	10.9	12.75
0.6	0.533	14.4	12.8	15.39
0.7	0.610	16.8	14.7	18.13
0.8	0.685	19.2	16.5	20.91
0.9	0.757	21.6	18.2	23.72
1.0	0.825	24.0	19.8	26.64

As will be seen by comparing the last three columns, much better agreement between the calculated and observed values is obtained by using weight normal concentrations.

[1] Morse and Frazer, *Am. Chem. J.*, **34**, 28 (1905); **38**, 212 (1907).

In other words we should, in calculating osmotic pressures, use the formula

$$P = C'RT,$$

where C' is the so-called Raoult concentration referred to one liter of solvent, instead of the equation $P = cRT$ in which the concentration, c, is expressed as volume concentration.

Sackur [1] and Porter [2] have similarly shown that by the use of the formula

$$P(V - b) = RT,$$

in which V represents the volume of solution in which one mole of solute is dissolved and b is a factor correcting for the volume occupied by the solute, we obtain results in agreement with experiment, as is seen by the data of Table XI.

TABLE XI

Comparison of Osmotic Pressures of Aqueous Sucrose Solutions at 0° Calculated by Sackur, with Measurements of Berkeley and Hartley

PV Observed	V	P in Atmospheres	PV Calculated
26.7	1.910	14	26.6
30.7	1.144	26.9	30.5
36.0	0.819	44.0	35.5
43.0	0.637	67.5	42.6
52.6	0.522	100.8	52.6
61.1	0.458	133.7	62.4

PV (calculated) in the above table is derived on the basis $b = 0.30$, so that PV (calculated) $= RT + bP = 22.4 + 0.30P$. The factor, b, however, is not a constant but varies with temperature and concentration, which variation is attributed to changes in hydration with a concomitant change in the volume occupied by the solute. This simple equation, however, fails to correct for the mutual attractions between solute and solvent molecules and hence its agreement with experimental results, in the cases to which it has been applied, can only be attributed to a fortuitous balancing of these effects. Moreover, as Schay [3] has pointed out, the equation of Sackur,

$$P = \frac{RTc}{1 - bc},$$

expressing V in terms of concentration, merely involves a correction in the denominator, and hence we may write it as

[1] *Z. physik. Chem.*, **70**, 477 (1910).
[2] *Trans. Farad. Soc.*, **13**, 128 (1917).
[3] *Z. physik. Chem.*, **106**, 378 (1923).

$$P = RTc(1 + bc),$$

which being a quadratic in c would be expected to give values in comparatively close agreement with experiment.

A great number of more complicated equations have been suggested by Bredig,[1] A. A. Noyes,[2] van der Waals,[3] Boltzmann,[4] Lorentz,[5] Berkeley and Hartley,[6] Callendar,[7] Fouard,[8] Jaeger,[9] Ehrenfest,[10] Jellinek,[11] and others, in which an analogy to the van der Waals' equation for gases has been sought that would correct for both volume and attraction factors. These equations are, however, very unsatisfactory, due to the possible multiplicity of forms that they may take, and the difficulties in ascribing any definite meaning to the empirical constants which they contain and which usually vary considerably.

O. Stern [12] has deduced an expression based on van der Waals' equation in which he considers a solution in which there is no molecular complex formation as a liquid mixture of two molecular species. He therefore expresses the partial osmotic pressures of the constituents individually by use of a relationship deviating somewhat from the original equation of van der Waals and derived [13] from the virial theorem. By correcting for the mutual attraction between solute and solvent Stern finally deduces the expression

$$P = \frac{RT}{V} + \frac{RT}{V^2}[b_1 - b_{12}(x_0 - x)] - \frac{1}{V^2}[a_1 - a_{12}(x_0 - X)].$$

Adverse criticism of this equation by van Laar [14] as regards the legitimacy of using van der Waals' equation as a basis for a general theory of solutions has been met by Jellinek,[15] who points out that the equation is applicable if we assume the additivity of the volumes of solvent and solute and of the volume correction factor b.

Recently, Schay,[16] by considering the observed osmotic pressure as resulting not from the bombardment of the dissolved particles on the membrane but rather as representing the difference in pressures of the solvent in the pure condition and in the solution, has extended the equation of Stern. This difference in pressures of solvent and solution he visualizes as being occasioned

[1] *Z. physik. Chem.*, **4**, 444 (1889).
[2] *Z. physik. Chem.*, **5**, 53 (1890).
[3] *Z. physik. Chem.*, **5**, 133 (1890).
[4] *Z. physik. Chem.*, **6**, 474 (1890).
[5] *Z. physik. Chem.*, **7**, 36 (1891).
[6] *Proc. Roy. Soc.*, **A 79**, 125 (1907).
[7] *Proc. Roy. Soc.*, **A 80**, 466 (1908); *Z. physik. Chem.*, **63**, 641 (1908).
[8] *Bull. Soc. Chim.*, [4] **13**, 784 (1913).
[9] *Ann. Physik*, [4] **41**, 854 (1913).
[10] *Proc. Akad. Weten. Amst.*, **17**, 1241 (1915); *Ann. Physik*, **48**, 369 (1915).
[11] *Z. physik. Chem.*, **92**, 169 (1918).
[12] *Z. physik. Chem.*, **81**, 441 (1913).
[13] Cf. Boltzmann, Gastheorie, II, p. 139.
[14] *Z. physik. Chem.*, **82**, 223 (1913).
[15] *Z. physik. Chem.*, **92**, 169 (1918).
[16] *Loc. cit.*

by the fact that the collisions per given area of the membrane due to the solvent particles in the solution are less frequent than those of the pure solvent over the same area, due to the relative sparsity of the former compared to the latter. This difference in the number of collisions on both sides of the membrane also accounts for the diffusion of solvent from the region of more frequent bombardment (solvent) into the solution. The final equations derived, however, despite their theoretical interest, offer no superiority over the simpler Sackur or Raoult formulæ in so far as practical application is concerned.

The above considerations have been limited to a discussion of solutions in which dissociation or complex formation is absent. The application of the kinetic theory to electrolytes has been less extended, due to the complexity involved in introducing factors which should express the variation of the electrical effects of the ions as a function of concentration.

P. Debye,[1] beginning with the assumptions that:

(1) Strong electrolytes are completely dissociated at all concentrations,

(2) The observed values in limiting laws (at zero concentration) may be attributed to mutual electric forces between the ions themselves and the molecules of the solvent,

has developed a mathematical theory of osmotic pressure based solely on kinetic grounds. By applying a consideration of the thermodynamic potential to the reasoning which had previously led him to deduce a relation for the freezing points of solutions, Debye [2] develops the expression

$$P = \gamma nkT + \varphi(n),$$

in which γ is the number of ions into which each molecule dissociates, n the number of molecules per cubic centimeter, k the Boltzmann constant $= 1.346 \times 10^{-16}$ erg, and T the absolute temperature. This expression is seen to give the osmotic pressure in the form of the classic formula corrected by an additive term, due to the electrostatic forces between the ions, which is a function of concentration. This function is further developed but its lengthy mathematical treatment need not be considered here.[3]

Despite the plausibility and numerous applications of the kinetic theory of osmotic pressure, no generally satisfactory relationship has as yet been derived. This failure is probably due not to any fundamental fault in the basic reasoning of the theory, but is rather to be attributed to the complexity of the forces involved in the phenomenon, which, in our present state of knowledge, do not allow exact formulation.

The Mechanism of Osmotic Pressure [4]

Theories Regarding the Nature of Semi-permeability: When one substance is dissolved in another, the solvent in the solution thus formed has a

[1] *Rec. trav. chim.*, **42**, 597 (1923).

[2] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[3] See Chapter XII.

[4] For a more detailed discussion of this subject, the reader is referred to the monograph on Osmotic Pressure by Alexander Findlay (Longmans, Green & Co., 1919), p. 94; the

free energy value, thermodynamic potential, or activity, different from that of the pure solvent. It is the tendency towards equalization of this difference and the attainment of an equilibrium condition which manifests itself in the production of an osmotic pressure when the two substances are separated by a semi-permeable membrane. This statement, however, tells us nothing of the mechanical details nor does it give us a view of the actual mechanism whereby this pressure is produced.

Experimental determinations of osmotic pressure have always been carried out with semi-permeable membranes. Numerous explanations have therefore been offered regarding the mechanism of this semi-permeability, but they all suffer from the fallacy that they are based on particular cases which they may satisfactorily explain, but lack any general application. We may thus mention

(1) the theory of M. Traube [1] who considered the action of the membrane as being that of an atomic sieve, allowing only molecules of certain dimensions to pass but preventing the passage of larger particles of solute;

(2) the theory of capillarity in which the membrane plays the part of a series of fine capillary tubes; [2]

(3) the chemical theory where actual combination of the membrane and solvent take place; [3]

(4) the theory of preferential solubility.[4]

It is probable that no single mechanism will explain all cases, varied mechanisms being possible, depending on the type of membrane used, whether colloidal, as $Cu_2Fe(CN)_6$, animal, as parchment, inert, as glazed porcelain plates, etc. In most cases it is probably a combination of causes, the resultant of which brings about the observed action. The nature of the mechanism of semi-permeability does not, however, enter into the theoretical considerations of osmotic pressure and, hence, is of no fundamental importance in such considerations.

The Nature of Osmotic Pressure: Regarding the nature of osmotic pressure, widely divergent views have been expressed. As a result of the analogy which has been shown to exist between gaseous and osmotic pressures, the view has suggested itself that osmotic pressure is due to the bombardment of the membrane by the solute and hence is a force whose nature depends on the dissolved substances. The objection to this kinetic theory, on the grounds that if this were the true origin of the phenomenon we would expect a flow of solvent from the solution, instead of into it, is irrelevant if we regard the case as analogous to the experiment of Ramsay cited previously (page 367). The number of collisions by solvent particles on a given area of the membrane per unit time will be less on the side of the solution than on the solvent side, and,

Symposium on the same subject in the *Transactions of the Faraday Society*, vol. 13, p. 133; Jellinek, *Physikalische Chemie*, vol. I.

[1] Traube, *Archiv. für Anat. Physiol. Med.* (1867), p. 87.

[2] Bigelow, *J. Am. Chem. Soc.*, **29**, 1675 (1907).

[3] Armstrong, *Proc. Roy. Soc.*, **B 81**, 94 (1909); **A 103**, 610 (1923); *Compt. rend.*, **177**, 257 (1923).

[4] L'Hermite, *Ann. chim. phys.*, [3] **43**, 420 (1855).

hence, there will be a flow of solvent into the solution until the number of these collisions on both sides of the membrane is equalized, or rather until the flow of solvent through the membrane is the same in both directions.

The other prominent theory of the nature of osmotic pressure considers the solvent as playing the chief rôle in osmosis. This hydrostatic theory, as it is called, attributes osmotic pressure to the entrance of solvent into the solution as a result of an attraction of solvent for solute. This entrance of solvent into the solution has been attributed to various factors. It has been explained [1] as due to the difference in surface tension of solvent and solution. Armstrong [2] has developed a theory according to which osmotic pressure in aqueous solutions results from hydrodynamic conditions, that is, the osmotic pressure of an aqueous solution is the hydraulic pressure exercised by the extra molecules of hydrone attracted into it by the complexes formed by the solute and hydrone. This theory is only a special case of the general idea that osmotic phenomena are due to an attraction between solute and solvent, resulting in the formation of definite and stable compounds such as hydrates in the case of aqueous solutions. This view has been championed by S. U. Pickering [3] who found that if a solution of propyl alcohol and water in a porous cup be surrounded by either the pure alcohol or water, there is always an osmosis of the pure liquid into the cup. This would indicate that the porous cup is not impermeable to any one constituent of the solution but rather to the hydrate formed in solution.

None of the theories advanced thus far seems to be entirely satisfactory. A satisfactory explanation of the nature of osmosis will most probably have to await a more thorough knowledge of the nature of solution, the dynamical properties of which are still insufficiently known.

Donnan's Membrane Equilibrium

One might expect "a priori" that a substance capable of diffusing through a membrane should distribute itself equally on both sides of this membrane independently of other substances that might be present. The presence, however, of another substance whose molecule is non-diffusible and which can dissociate into a diffusible and non-diffusible ion will cause an unequal distribution of an electrolyte towards whose molecule and ions the membrane is permeable. The theory advanced by F. G. Donnan [4] in 1910 to cover this distribution of ions has found a far-reaching and successful application in the fields of colloidal and physiological chemistry where we often meet the conditions bringing about this phenomenon.

We can best develop this theory by considering a specific case as has been

[1] Traube, *Ber.*, **17**, 2294 (1884); *Phil. Mag.*, [6] **8**, 704 (1904). Moore, *Phil. Mag.*, [5] **38**, 279 (1894).

[2] *Proc. Roy. Soc.*, **A 103**, 610 (1923); *Compt. rend.*, **176**, 1892 (1923). Gellet, *Compt. rend.*, **177**, 257 (1923).

[3] *Ber.*, **24**, 3639 (1891); *Nature*, **55**, 515 (1900).

[4] Address to London Physiological Society, Dec., 1910.

done by Donnan in his original article.[1] Let us consider a membrane (MM⁻, Fig. 28*a*) impermeable both to the molecule of a salt NaR (e.g., the sodium salt of congo red) and the anion R^- which it gives on dissociation, permeable to the cation, Na^+, as well as to the molecules or ions of other salts. This impermeability of the membrane towards any species of dissolved substance may be considered merely as a result of the small diffusion velocity of the species in question through the membrane due to its size, which permits us to neglect it compared with the diffusion velocities of the other substances in question. The true nature of this impermeability need not be considered. If, now, we imagine a solution of the salt NaR to be on one side of the membrane, (1), and a solution of diffusible NaCl to be on the other, (2), the latter will diffuse through the membrane to side (1) until an equilibrium is reached as

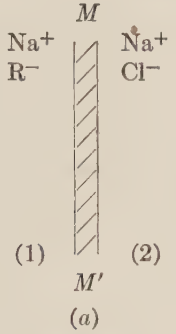


FIG. 28*a*

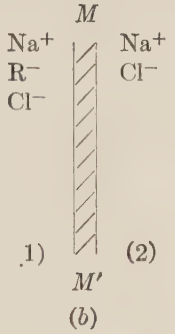


FIG. 28*b*

represented by the arrangement (Fig. 28*b*). This equilibrium is characterized by the condition that the maximum work obtained in an isothermal and reversible transference of an infinitesimal amount of sodium ions, δn, in one direction is equal to that expended in a similar transportation of δn chlorine ions in the same direction. The algebraic sum of the total work done (i.e., the decrease in free energy) must, therefore, be equal to zero. The work obtained in the transport of δn moles of Na^+ from the side (1) where its concentration is $[Na^+]_1$ to side (2) where it is $[Na^+]_2$ will be equal to

$$\delta n R T \ln \frac{[Na^+]_2}{[Na^+]_1}$$

and, similarly, for the chlorine ion this work is

$$\delta n R T \ln \frac{[Cl^-]_2}{[Cl^-]_1}.$$

But, at equilibrium, as stated above,

[1] Donnan, *Z. Elektrochem.*, **17**, 572 (1911). Lewis, System of Physical Chemistry, Longmans, Green & Co. (1919), vol. 2, p. 275.

$$\delta nRTln\frac{[Na^+]_2}{[Na^+]_1} + \delta nRTln\frac{[Cl^-]_2}{[Cl^-]_1} = 0, \qquad [1]$$

whence we derive the relationship

$$[Na^+]_2.[Cl^-]_2 = [Na^+]_1.[Cl^-]_1, \qquad [2]$$

i.e., the products of the permeable anions and cations on each side of the membrane are equal. No consideration need be taken, in the above derivation of the work necessary for this virtual change in the system, of any potential difference between [1] and [2] inasmuch as equal quantities of both positive and negative electricity have been transferred. The above quantities derived for the work terms in equation [1] assume the applicability of van't Hoff's osmotic pressure law which assumption is valid, since we are limiting ourselves to a consideration of dilute solutions.

We can derive a similar expression for the equilibrium conditions with respect to the undissociated NaCl by considering an infinitesimal, isothermal, reversible transference of δn moles from [2] to [1]. Assuming, here also, the applicability of the van't Hoff generalization, we have

$$\delta nRTln\frac{[NaCl]_2}{[NaCl]_1} = 0 \qquad [3]$$

or

$$[NaCl]_1 = [NaCl]_2, \qquad [4]$$

i.e., the concentration of the undissociated molecules to which the membrane is permeable is the same on both sides of the membrane. Combination of equations [2] and [4] leads to the expression of the mass action law for ionized substances

$$\frac{[Na^+].[Cl^-]}{[NaCl]} = \text{Constant},$$

which we know to be non-applicable, assuming the accuracy of the values for the degree of dissociation as derived from conductivity measurements. The difficulty need not disturb us, however, as it rests on an assumption which we now know to be inexact.

Returning to equation [2], it is evident that to obtain electroneutrality in the solution, $[Na^+]_1$ must equal $[R^-] + [Cl^-]_1$ and $[Na^+]_2 = [Cl^-]_2$, and hence we can write equation [2] as

$$[Na^+]_1.[Cl^-]_1 = [Na^+]_2^2 = [Cl^-]_2^2,$$

whence it follows that neither $[Na^+]_1 = [Na^+]_2$ nor does $[Cl^-]_1 = [Cl^-]_2$, since $[Na^+]_1 \neq [Cl^-]_1$, which follows from the above statement

$$[Na^+]_1 = [R^-] + [Cl^-]_1.$$

To obtain a better and more quantitative statement of the above conditions let us assume

(1) Complete dissociation of NaR and NaCl.

(2) Equal volumes of liquid on both sides of the membrane, which we may represent diagrammatically in Fig. 29 thus:

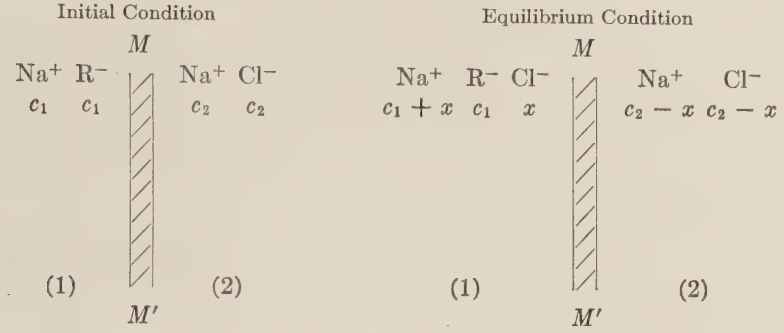


FIG. 29

in which the molar ionic concentrations of the various constituents are represented by the algebraic symbols, and x represents the concentration of Na^+ and Cl^- which have diffused through the membrane.

If we now substitute these symbols for the concentrations, in the equation

$$[Na^+]_1 . [Cl^-]_1 = [Na^+]_2{}^2 = [Cl^-]_2{}^2,$$

we obtain

$$(c_1 + x)(x) = (c_2 - x)^2,$$

whence

$$x = \frac{c_2{}^2}{c_1 + 2c_2}.$$

Dividing through by c_2, we get

$$\frac{x}{c_2} = \frac{c_2}{c_1 + 2c_2},$$

which relation gives us the fraction of NaCl, $\frac{x}{c_2}$, initially present in (2) that has diffused to (1) in terms of the initial concentrations of NaR and NaCl. The following table shows this variation in the distribution of NaCl as a function of the initial concentrations.

As will be seen from column (4), the amount of NaCl diffusing through the membrane will vary from 50 per cent of the original amount present, when the concentration of NaR is negligible, to only 1 per cent, when the concentration of NaCl is but 1/100 of that of the NaR. The same equilibrium conditions result, of course, regardless of whether we start with NaCl in (2) alone or on both sides of the membrane, or whether we start with both NaR and NaCl on one side of the membrane only. We thus see that the influence of an electrolytically dissociating substance on the permeability of a diffusible substance, despite the non-permeability of the molecule and one ion of the former, is

very marked, and may, if present in sufficient quantity, even prevent the normal diffusion of the latter substance.

TABLE XII

DISTRIBUTION OF NaCl AT EQUILIBRIUM

Initial Concentration of NaR in (1)	Initial Concentration of NaCl in (2)	Initial Ratio of Concentration of NaR to NaCl	Percentage of NaCl Transferred from (2) to (1)	Distribution Ratio of NaCl between (2) and (1)
c_1	c_2	c_1/c_2	$\frac{x}{c_2} \cdot 100$	$\frac{c_2 - x}{x}$
0.01	1	0.01	49.7	1.01
0.1	1	0.1	47.6	1.1
1	1	1	33	2
1	0.1	10	8.3	11
1	0.01	100	1	99

As Donnan pointed out, this phenomenon must play an important rôle in physiological processes where the presence of the non-dialyzable anions of the salts of the proteins, etc., may modify the diffusibility of ordinary inorganic substances which normally are capable of diffusing through the cell membrane.

Physiological investigations have led to the view that the membranes of many cells show a peculiar elective permeability for ions which is not related to any colloidal character of these ions. Thus Höber[1] concluded that the cells in general showed a variation in permeability towards the anions and cations. The problem of the selective adsorption of drugs by the cells and the influence of electrolytes on this adsorption is but one of the many practical applications of the Donnan Membrane Equilibrium in the medical sciences.

Osmotic Pressure and Membrane Equilibrium: As a result of the unequal distribution of NaCl on the two sides of the membrane considered above, the observed value of the osmotic pressure of NaR is not the true pressure, since the latter is opposed by the pressure exerted by the excess NaCl on the other side of the membrane. Assuming complete dissociation and equal volumes of solution on both sides of the membrane and letting c_1 be the concentration of NaR, P_0, the true osmotic pressure of the NaR, will be given by the equation

$$P_0 = 2c_1RT,$$

since the total concentration of ions from c_1 moles of NaR is $2c_1$, each molecule of NaR dissociating into Na^+ and R^-. If P is the counter pressure due to the unequal distribution of NaCl,

$$P = 2(c_2 - x - x)RT,$$

[1] Höber, Physikalische Chemie der Zelle und Gewebe. Leipzig, 1922.

since the concentration of ions from the NaCl in (2) is $2(c_2 - x)$ and in (1) is $2x$, and hence the excess concentration in (2) is $2(c_2 - x - x)$.

The observed osmotic pressure

$$P_1 = P_0 - P = 2RT[c_1 - (c_2 - 2x)],$$

whence

$$\frac{P_1}{P} = \frac{c_1 - (c_2 - 2x)}{c_1}.$$

But

$$x = \frac{c_2^2}{c_1 + 2c_2},$$

which, when substituted in the above equation, gives

$$\frac{P_1}{P_0} = \frac{c_1 + c_2}{c_1 + 2c_2}.$$

The numerical relationships between the observed osmotic pressures and those exerted in the absence of an electrolyte, as derived from the last equation, are given below (Table XIII).

TABLE XIII

OSMOTIC PRESSURE RATIOS

$\frac{c_1}{c_2}$	$\frac{P_1}{P_0}$	$\frac{c_1}{c_2}$	$\frac{P_1}{P_0}$
0.1	0.92	2	0.60
1	0.67	10	0.52

The observed osmotic pressure of an electrolytically dissociated non-dialyzing substance is thus lowered by the addition of an electrolyte with a common ion, as has been experimentally verified.[1]

Effect of an Electrolyte without Common Ion: The above-described effect in the case of NaCl and NaR is not limited to such cases where we have an ion in common between the electrolyte and non-dialyzing substance, but may be extended by a similar treatment to cases such as NaR and KCl where no such common ion is present.

Beginning with initial concentrations as represented in Fig. 30, the ions of KCl will diffuse from (2) to (1) and the ions of NaCl thus produced in (1) will then diffuse from (1) to (2), to bring about the equilibrium state represented also in Fig. 30. The algebraic subscripts denote ionic concentrations. To satisfy the conditions necessary for electric neutrality, z must be equal to $x - y$, i.e., z, the number of moles of Na^+ transferred from (2) to (1), must equal

[1] Donnan and Harris, *J. Chem. Soc.*, 99, 1554 (1911). Donnan and Allmand, *ibid.*, 105, 194 (1914). Donnan and Garner, *ibid.*, 115, 1313 (1919). Biltz, *Z. physik. Chem.*, 83, 625 (1913).

the algebraic sum of x, the number of moles of K^+ transferred from (2) to (1) minus y, the number of moles of (Cl^-) transferred from (2) to (1).

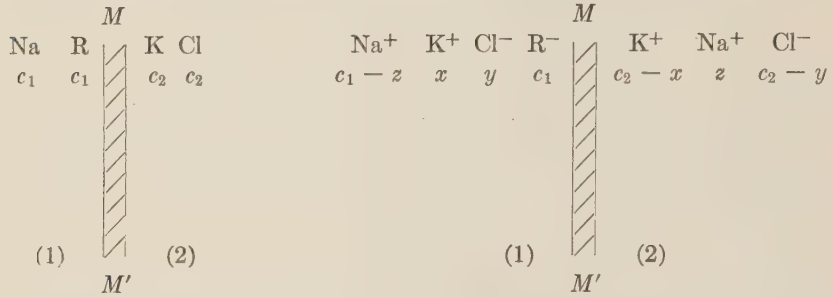


FIG. 30

By a consideration of the work done in small virtual isothermal and reversible changes in the system, we obtain three pairs of variations:

1. $$\begin{cases} \delta n \text{ mol. } Na^+ & (1) \rightarrow (2), \\ \delta n \text{ mol. } K^+ & (2) \rightarrow (1), \end{cases}$$

in which

$$\delta n RT ln \frac{[Na^+]_1}{[Na^+]_2} + \delta n RT ln \frac{[K^+]_2}{[K^+]_1} = 0$$

and

$$\frac{[Na^+]_1}{[Na^+]_2} = \frac{[K^+]_1}{[K^+]_2}.$$

2. $$\begin{cases} \delta n \text{ mol. } Na^+ & (1) \rightarrow (2), \\ \delta n \text{ mol. } Cl^- & (1) \rightarrow (2), \end{cases}$$

$$\frac{[Na^+]_1}{[Na^+]_2} = \frac{[Cl^-]_2}{[Cl^-]_1}.$$

3. $$\begin{cases} \delta n \text{ mol. } K^+ & (1) \rightarrow (2), \\ \delta n \text{ mol. } Cl^- & (1) \rightarrow (2), \end{cases}$$

$$\frac{[K^+]_1}{[K^+]_2} = \frac{[Cl^-]_2}{[Cl^-]_1}.$$

Combining these three results and substituting values of the concentrations, we get

$$\frac{[Na^+]_1}{[Na^+]_2} = \frac{[K^+]_1}{[K^+]_2} = \frac{[Cl^-]_2}{[Cl^-]_1} = \frac{c_1 + c_2}{c_2} = r,$$

which relation gives us the ratio of the concentrations of any of the dialyzable ions on the two sides of the membrane.

To illustrate this distribution, let us consider the case in which $\frac{c_1}{c_2} = 100$ and therefore $r = 101$. The changes taking place will be:

1. A diffusion of 99 per cent of the K^+ initially present in (2) to (1).
2. A diffusion of only 1 per cent of the Cl^- initially present in (2) to (1).
3. A diffusion of 1 per cent of the Na^+ initially in (1) to (2).

The presence of the NaR has markedly affected the normal distribution of KCl on the two sides of the membrane, having produced a preferential effect whereby practically all the cations of the diffusible electrolyte have been attracted through the membrane and hence show an extraordinary permeability, while the anions on the other hand are expelled.

Hydrolytic Decomposition by Membranes: If we consider the effect of having an aqueous solution of NaR on one side of the membrane and pure water on the other, we find that the NaR will be hydrolyzed. The Na^+ will pass through the membrane since the latter is permeable to it, and in order to maintain electric neutrality, an equivalent amount of (OH^-) from the hydrolytic dissociation of water will diffuse in the same direction, so that the initial and final conditions are represented by Fig. 31. In other words, side (1) will be-

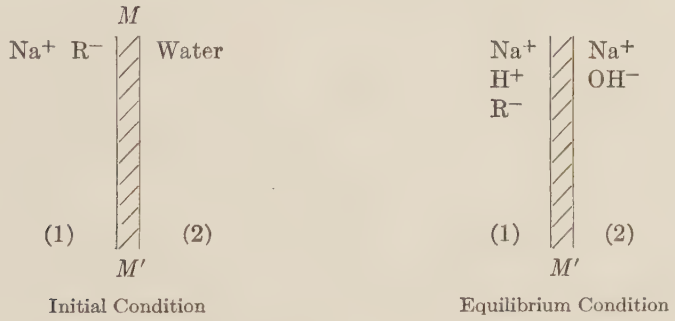


FIG. 31

come acid while side (2) will become alkaline, the salt NaR having been hydrolyzed in the process. By following the same considerations as were employed in the development of the previously discussed processes, the extent of this hydrolysis can be expressed by the relation

$$x = \sqrt[3]{K_w c_1},$$

where x is the concentration of the Na^+ that diffuses through the membrane, K_w the ionization constant of water, and c_1 the original concentration of NaR. This equation is derived on the assumption that (1) and (2) occupy equal volumes. If, however, the volume of (2) is v times as great as that of (1), we obtain the corresponding equation

$$x = \sqrt[3]{K_w v^2 c_1}.$$

Despite the small extent of this hydrolysis, it must take place wherever we have a membrane on one side of which is an electrolyte only one of whose dissociation products can diffuse through the membrane into the water on the other side as, e.g., a solution of $K_4Fe(CN)_6$ with a $Cu_2Fe(CN)_6$ membrane. Not only will this hydrolysis affect the observed osmotic pressures of electrolytic colloids but this process also explains the observed removal by dialysis of only one of the ions of an electrolyte adsorbed by a gel. In this case the gel acts as a membrane and if it is permeable to only one of the ions of the electrolyte, this one will pass through and, by continued dialysis, be entirely removed, leaving the other in the form of an acid or base, depending on whether it was the anion or the cation of the electrolyte originally present.

Donnan's theory of membrane equilibrium has also been widely and successfully applied in consideration of the membrane potential difference existing when equilibrium, as brought about by the membrane, has been attained.[1] Inasmuch, however, as this phase of the subject belongs to a consideration of colloids rather than of the laws of dilute solutions, it will not be considered further here.

[1] See, for example, Loeb, Proteins and the Theory of Colloidal Behaviour, McGraw-Hill Co., 1921.

CHAPTER VIII

HOMOGENEOUS EQUILIBRIA

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Our knowledge of equilibrium and of the "Law of Mass Action" has its beginnings very early in the history of the science, originating in speculations of early investigators as to the cause of chemical action. In the "Tables of Affinity" of Bergmann [1] we find no conception of equilibrium save that of the reversibility of reactions under different physical conditions, as shown by the somewhat different order of the "Affinities" of the elements "in fire" and "in water." Wenzel [2] suggested shortly afterwards that quantity or concentration as well as chemical nature affected the *rate* of chemical action, but this suggestion, which might have had important results, was apparently unnoticed until long afterwards.

The next important step in the development of the subject came in 1799, when Berthollet [3] read certain papers on chemical affinity in which he suggested that large quantity of a material might overcome a weak affinity, and pointed out that the sodium carbonate deposits of Egypt might have been formed from calcium carbonate and salt, the great masses of the latter serving to reverse the usual reaction. This is certainly very nearly a "mass law," but unfortunately Berthollet himself confused the situation by maintaining that mass could affect not only the direction of a reaction but also the ratio in which the substances combine. This brought him into immediate conflict with the law of definite proportions, just then being placed on a firm experimental basis, and in the ensuing controversy Berthollet's conclusions were discredited.

The next advances began to appear, as has been true so frequently in all science, when quantitative experimental investigations began to supplement hypothetical assertions. The investigations of Rose [4] suggested the importance of quantity in affecting chemical action: Wilhelmy [5] made the first quantitative study of the *rate* of a chemical reaction; Malaguti [6] showed that many reactions are reversible, and others added individual facts upon which a theory could be built.

[1] T. Bergmann, De Attractionibus Electtior's, Upsala (1775).
[2] C. F. Wenzel, Lehre von der Verwandschaft, Dresden, 28 (1777).
[3] C. L. Berthollet, *Memoirs National Institute*, **3** (1799).
[4] *Pogg. Ann.*, **55**, 417 (1842); **82**, 545 (1851); **94**, 481 (1885).
[5] *Pogg. Ann.*, **81**, 413, 499 (1850).
[6] *Ann. Chim. Phys.*, (3) **37**, 198 (1853).

Finally Berthelot and St. Gilles[1] carried out an extensive investigation of the equilibrium between acetic acid, ethyl alcohol, ethyl acetate, and water, and showed that their data could be represented mathematically by the identical expression which the present "Mass law" would give for this reaction.

It remained, however, for Guldberg and Waage[2] to enunciate the generalization which expresses essentially what is commonly called the "law of mass action" of to-day, and to point out clearly the general reversibility of chemical reactions, and the conditions which exist at equilibrium. Guldberg and Waage stated essentially that the rate at which a substance reacts is proportional to its "active mass," and that the rate of a chemical reaction is proportional to the product of the active masses of the substances reacting; thus, if we consider the reaction,

$$A + B = C + D, \tag{1}$$

the rate of the reaction at any given time, from left to right, is given by the expression

$$V_1 = K_1 \times A_A \times A_B, \tag{2}$$

where A_A, etc., represent the active masses of A and B present at that time.

If the reaction is reversible, the rate of the opposing reaction is then

$$V_2 = K_2 \times A_C \times A_D. \tag{3}$$

If both reactions occur simultaneously, a condition will eventually be reached in which $V_1 = V_2$, when, from equations (2) and (3), we have

$$\frac{K_1}{K_2} = K = \frac{A_C \times A_D}{A_A \times A_B}. \tag{4}$$

Equilibrium is thus considered as a dynamic condition, in which two opposing reactions occur at equal rates, and the "equilibrium constant," K, is simply the ratio of the two separate velocity proportionality constants.

Guldberg and Waage recognized the difficulty introduced by the use of the term "active mass," and pointed out that apparently "molecular concentration" could be substituted therefor in the case of dissolved or gaseous substances, and that the active mass of a solid may be considered as constant.

The Condition of Equilibrium in a Chemical Reaction

The Reversibility of Chemical Reactions: Since the time of Guldberg and Waage, numerous experimental investigations have demonstrated the reversibility of particular chemical reactions, and have determined the condition of equilibrium for them under different conditions of temperature and pressure. Furthermore, the application of the principles of thermodynamics to the energy changes accompanying chemical reactions has led to very noteworthy ad-

[1] *Ann. Chim. Phys.*, (3) 65, 385 (1862); 66, 5 (1862); 68, 225 (1863).

[2] *Forhandlinger i Videnskabs-Selskabet i Christiania*, 35, 92, 111 (1864). *Etudes sur les affinites chemiques*, Christiania, 1867.

vances in our knowledge of the relations existing at equilibrium, and many technical chemical processes of the greatest importance owe their existence to these advances in theory. Nevertheless, there has existed in the literature frequent confusion concerning the fundamental theories underlying the subject. Simplifying assumptions have been made when they could not be expected to be valid; and "laws" containing these assumptions have been widely used, sometimes without apparent realization of the nature of the assumptions involved. The failure of experimental data to conform to these simplified principles has then in many cases led to an unjustified lack of confidence in the fundamental theories involved. Instead, therefore, of considering the subject historically since the time of Guldberg and Waage, it seems preferable to treat in this section the subject of chemical equilibrium from a broad general viewpoint, and to illustrate its actual application to particular cases in a later section. In this treatment we shall speak continually of "reversible" reactions. In the older literature this term is frequently used with reference only to reactions which may have been experimentally carried out in opposite directions. Whereas this use of the term may serve as a convenient method of distinguishing such reactions from those which go to apparent completion in one direction, there is no reason to believe that any reaction is not reversible, at least for the purpose of theoretical considerations. The fact that an equilibrium may lie so far on the side of complete reaction in one direction as to fail of experimental measurement, or the fact that the *rate* of chemical reaction in a given case may be so slow as to prevent the establishment of equilibrium under the conditions investigated, need not prevent us from considering the condition which must prevail at equilibrium in these same reactions. We shall, therefore, consider every reaction as reversible, and as proceeding eventually to a state of equilibrium, which will be determined by the temperature, the pressure (and perhaps other energy factors), and the proportions of the reacting substances.

Chemical Equilibrium from the Standpoint of Kinetics: As indicated in the introductory paragraphs, the "Mass law" as derived by Guldberg and Waage was based essentially upon consideration of the kinetics of chemical reactions. It may be noted that for a reaction between dilute gases a statement similar to the equation (4) may be derived from theoretical considerations, based upon the kinetics of moving particles and simple assumptions concerning the relation between the collisions of the reacting species and their combination.

Let us consider the reaction

$$A + B = C + D,$$

where A, B, C, and D are dilute gases. Let us then assume that the number of reactions per unit of time between A and B is proportional to the number of collisions of molecules of A and B in the same time interval. The number of collisions is obviously proportional to the product of the number of molecules of A and the number of molecules of B present in unit volume, or to the product

of their partial pressures; thus $N_c = K \times P_A \times P_B$. Since the rate of the reaction between A and B is assumed to be proportional to N_c, we have

$$V_1 = K_1 \times P_A \times P_B,$$

where V_1 is the rate of reaction at a given time, and P_A and P_B the partial pressures of A and B at that time.

Similarly,

$$V_2 = K_2 \times P_C \times P_D.$$

At equilibrium $V_1 = V_2$, hence

$$\frac{K_1}{K_2} = K = \frac{P_C \times P_D}{P_A \times P_B}. \tag{6}$$

If the partial pressures are taken as the "active mass" which is in accordance with the assumptions of Guldberg and Waage, equation (6) is identical with equation (4).

Let us consider the general reaction

$$aA + bB + \cdots = cC + dD \cdots.$$

Since the number of collisions of a molecules of A and b molecules of B per unit of time is given by $N_c = K \times P_A{}^a \times P_B{}^b$, we arrive, by reasoning similar to that just given, at the expression

$$\frac{K_1}{K_2} = K = \frac{P_C{}^c \times P_D{}^d \cdots}{P_A{}^a \times P_B{}^b \cdots}. \tag{7}$$

This equation will be later derived for reactions between dilute gases, from thermodynamic considerations.

The equilibrium constant may thus be regarded, in accordance with the views of Guldberg and Waage, as the ratio between the two velocity constants. Obviously, it should then be calculable from measurements of the two separate reactions. This has, however, seldom been done, as the direct determination of the equilibrium constant is usually more readily accomplished than the measurement of the velocity constants. The relation expressed in equation (7) has been used, however, to determine the *velocity* constant of a reaction from measurement of the equilibrium constant, and the velocity of the reverse reaction.[1]

Since the equilibrium constant is, as shown above, determined by the nature of the reaction as expressed in the equation, while the velocity of the reaction frequently follows a quite obscure course, it seems better on the whole to consider the equilibrium conditions from the thermodynamic view rather than from the kinetic view.

Chemical Equilibrium from the Standpoint of Thermodynamics: The laws of thermodynamics give many relations between the energy changes occurring

[1] For an example of this compare Bodenstein, *Z. physik. Chem.*, **100**, 68 (1922).

in "reversible processes" or, in other words, processes conducted in such a way that the system is maintained throughout in a state essentially that of equilibrium; or, in such a way that the direction of the change can be reversed by the expenditure of an infinitesimal quantity of energy. If we grant that chemical reactions are reversible, and that a condition of equilibrium may exist between the reacting constituents, it is clear that we may apply to such reactions the laws relating to reversible processes, provided always that we may conceive of a mechanism by which the change can be carried out under proper conditions of equilibrium. Since the energy changes accompanying a reversible process are determined in general by the initial and final states of the system, the deductions of thermodynamics have the advantage that they are independent of the mechanism by which the change is brought about. This, of course, involves the drawback that proof of the mechanism of the change cannot be derived from the final results by thermodynamic reasoning. In applying the principles of thermodynamics to a chemical reaction, therefore, we are concerned with the relations which exist between the proportions of the reacting substances *at the equilibrium condition,* and not with the mechanism by which the condition of equilibrium was attained.

In order to measure the maximum work and the free energy decrease accompanying chemical reactions we shall frequently wish to carry out a process involving the transfer of a gas from one pressure to another, or of a solute from one concentration to another, the process being conducted reversibly throughout.

If we consider a mol. of gas at pressure P_1, the maximum work A which the gas can do in changing to pressure P_2 is given by the equation

$$A = \int_{V_1}^{V_2} P dV. \tag{8}$$

Remembering that

$$\int x dy + \int y dx = xy,$$

we may write equation (8)

$$A = P_2V_2 - P_1V_1 - \int_{P_1}^{P_2} V dp. \tag{9}$$

Now the free energy increase ΔF accompanying a given change is related to the maximum work by the equation

$$-\Delta F = A - \Sigma P \Delta V, \tag{10}$$

where $\Sigma P \Delta V$ is the net increase in the pressure-volume product which accompanies the change in question.

Combining equations (9) and (10), we obtain

$$\Delta F = \int_{P_1}^{P_2} V dP. \tag{11}$$

If the gas is a perfect gas, we have $PV = RT$, and $P_2V_2 = P_1V_1$, so that

$$A = -\Delta F = RT ln \frac{V_2}{V_1} = RT ln \frac{P_1}{P_2}. \tag{12}$$

A and $-\Delta F$ are, thus, in this case identical; they are also identical for any change in which the volume is constant; and they are frequently very nearly equal numerically. Nevertheless it is ΔF and not A that is the thermodynamic quantity of greatest importance in considering the condition of equilibrium, for the essential condition of a system in equilibrium is that $\Delta F = 0$ (see Chapter II).

If chemical reactions were in general carried out at constant volume, it would be evidently immaterial whether we calculate A or ΔF, as the two are then equal, but it is nearly always the pressure that is maintained constant and not the volume, so that A and ΔF are apt to differ numerically. We shall, therefore, consider only the free energy increase accompanying given changes in state and not the maximum work.

If we wish to consider the free energy increase accompanying the transfer of a solute from one concentration to another, the calculation may be made as follows: If the solute obeys Henry's law, that is, if its partial pressure above the liquid is proportional to its mol. fraction, we may transfer it from one concentration to another by a three step process.

1. The first step will be to vaporize one mol. of it from a very large quantity of the solution of mol. fraction X_1 at its partial pressure P_1 $(= KX_1)$. Since the system is in equilibrium during this process, $\Delta F_1 = 0$.

2. We may then change the pressure reversibly from P_1 to P_2 $(= KX_2)$. The free energy increase for this step is (equation 11)

$$\Delta F_2 = \int_{P_1}^{P_2} V dP. \tag{13}$$

3. We may then introduce the vapor into a large quantity of the solution whose mol. fraction is X_2, and since this also involves a system in equilibrium, $\Delta F_3 = 0$.

The entire free energy increase is then given by ΔF_2, and if the vapor obeys the gas laws, we have

$$\Delta F = RT \ln \frac{P_2}{P_1} = RT \ln \frac{X_2}{X_1}. \tag{14}$$

Similarly, if the solution obeys Henry's law, and is also so dilute that the mol. fraction is proportional to its molecular concentration, or to its molality (concentration in mols. per 1000 grams of solvent), we may write, for a change from C_1 to C_2 or from M_1 to M_2,

$$\Delta F = RT \ln \frac{C_2}{C_1}; \qquad \Delta F = RT \ln \frac{M_2}{M_1}. \tag{15}$$

The relations which must exist at equilibrium in a chemical reaction may now be simply derived for cases in which the laws of perfect gases or of perfect solutions are valid.

Derivation of the Mass Law for a Gaseous System: Let us consider the following reaction between the substances A, B, C, and D, etc., according to the equation

$$aA + bB \cdots = cC + dD \cdots.$$

Let us take two different equilibrium systems I and II, at the same temperature, produced by allowing two different mixtures of the reacting substances to come to equilibrium, and let these two systems be so large that removal of small quantities of the reacting species does not alter their composition appreciably. Furthermore, let us suppose the two systems to be contained in vessels provided with membranes permeable only to A, B, C, and D, respectively, leading to cylinders provided with pistons, by means of which any given component of the mixture may be withdrawn or added to either system.

Step (1). Let us withdraw from reservoir (I) a mols. of A and b mols. of B at the partial pressures P_{1_A} and P_{1_B}, at which they are present in the equilibrium system (I). The free energy increase for this step is evidently zero, since the condition of equilibrium is not measurably disturbed.

Step (2). Let us change, reversibly, the pressures of the two gases to P_{2_A} and P_{2_B}, at which they exist in the second equilibrium system. The free energy increase for this step is evidently, since the gas laws are obeyed,

$$\Delta F_1 = aRTln\frac{P_{2_A}}{P_{1_A}} + bRTln\frac{P_{2_B}}{P_{1_B}}. \tag{16}$$

Step (3). We may now introduce the gases into the equilibrium system II, and since this does not measurably disturb the equilibrium, we have again zero free energy increase.

Steps (4), (5), and (6). Let us carry out a similar series of steps by which we remove c mols. of C and d mols. of D from system II, change their partial pressures from P_{2_C} and P_{2_D} to P_{1_C} and P_{1_D}, and introduce them into system I. The total free energy increase is then, as above,

$$\Delta F_2 = cRTln\frac{P_{1_C}}{P_{2_C}} + dRTln\frac{P_{1_D}}{P_{2_D}}. \tag{17}$$

Steps 1, 2 and 3, and 4, 5, and 6 are supposed to be carried out at corresponding times, and so slowly that the A and B removed from system I react in system II to replace the C and D which have been removed therefrom, which in turn react in system I to form A and B. If this has been the case, the entire composition of each system is just what it was at the beginning of the process, and as each step has been carried out isothermally and reversibly, the total free energy increase must be zero (Chapter II).

Therefore,

$$\Delta F_1 + \Delta F_2 = 0,$$

and, from equations (16) and (17),

$$RTln\frac{P_{2_A}}{P_{1_A}} + bRTln\frac{P_{2_B}}{P_{1_B}} + cRTln\frac{P_{1_C}}{P_{2_C}} + dRTln\frac{P_{1_D}}{P_{2_D}} = 0. \tag{18}$$

Or, rearranging,

$$RT\ln\frac{P_{2_C}^{c}\times P_{2_D}^{d}\cdots}{P_{2_A}^{a}\times P_{2_B}^{b}\cdots}=RT\ln\frac{P_{1_C}^{c}\times P_{1_D}^{d}\cdots}{P_{1_A}^{a}\times P_{1_B}^{b}\cdots}, \tag{19}$$

whence

$$\frac{P_{2_C}^{c}\times P_{2_D}^{d}\cdots}{P_{2_A}^{a}\times P_{2_B}^{b}\cdots}=\frac{P_{1_C}^{c}\times P_{1_D}^{d}\cdots}{P_{1_A}^{a}\times P_{1_B}^{b}\cdots} \tag{20}$$

or, since these were any two sets of equilibrium pressures,

$$\frac{P_C{}^{c}\times P_D{}^{d}\cdots}{P_A{}^{a}\times P_B{}^{b}\cdots}=K. \tag{21}$$

Equation (21) is identical, for a dilute gaseous system, with the mass law of Guldberg and Waage, and with that obtained previously (equation 7) from kinetic considerations.[1]

Equation (21) was derived for a dilute gaseous system. If, however, we consider the reaction as occurring between substances in solution, we may readily derive a similar equation for any substance in solution whose vapor obeys Henry's law and the simple gas law. The procedure is identical with that employed in deriving equation (21) except that the two equilibrium systems are liquid, and the transfer of each solute from one concentration to the other is done by first vaporizing it from the solution. The free energy change for each mol. transferred is given by equation (14), and the final result is that

$$K=\frac{X_C{}^{c}\times X_D{}^{d}\cdots}{X_A{}^{a}\times X_B{}^{b}\cdots}. \tag{22}$$

Similarly, if the solution is quite dilute, we may write (compare equation 15)

$$K=\frac{C_C{}^{c}\times C_D{}^{d}\cdots}{C_A{}^{a}\times C_B{}^{b}\cdots}. \tag{23}$$

Equations (22) and (23) may also be derived by consideration of the osmotic work involved in the transfer of material from one concentration to another, making use of the relation that $P_0 = CRT$, where C is the molecular concentration.

Equations (21), (22) and (23) constitute the mass laws ordinarily employed. They express the relations which may be expected to exist at equilibrium at any given temperature, provided the reacting substances are gases sufficiently dilute to obey the gas laws, or ideal or sufficiently dilute solutions. Now the gas laws are actually approximately valid for a large number of gases under conditions in which they are apt to occur in chemical reactions, but the ideal

[1] *Note:* In writing mass law expressions, it has become an established convention to write in the *numerator* the partial pressures, concentrations, etc., of the substances appearing on the right hand side of the chemical equation. In order to avoid confusion, this procedure should be rigidly followed.

solution laws are valid for only a very small fraction of the solutions which are apt to be employed. If the simple laws are not assumed, it would be necessary to know the "equation of state" of each reacting substance in order to derive a statement of the concentrations which might be expected to prevail under different conditions of equilibrium. The derivation of a simple mass law in terms of partial pressures, concentrations, etc., in the case of a general reaction between gases, liquids and solids, and assuming no equations of state, cannot be accomplished. For many purposes it is convenient to consider the question of equilibrium in chemical reactions from the standpoint of the *activities* [1] of the reacting species.

The activity is defined essentially by the equation

$$F_A = RTln a_A + C_A, \tag{24}$$

where F_A is the molal free energy of the substance A under given conditions, a_A is its activity, and C_A is a constant which may be arbitrarily defined. (In *Lewis and Randall*, C_A is called F_0, "the molal free energy in the standard state," the "standard state" of a substance being selected arbitrarily for different types of reaction.) A full discussion of this useful function will not be given here, but it may be pointed out, in order to illustrate the general nature of the "activity," that the activity of a perfect gas is equal to its pressure, and for any actual gas the activity approaches the pressure as the gas becomes dilute; the activity of a solute is equal to its mol. fraction when the solution is sufficiently dilute. In the case of aqueous solutions the activity is frequently defined to approach the molality instead of the mol. fraction when the solution becomes dilute. If it is desired to visualize the term, it may perhaps be thought of as the "apparent concentration" or "effective concentration" which may not be identical with the actual concentration.

The increase in free energy when a substance changes from one set of conditions to another is given from equation (24) by the equation

$$\Delta F_A = RTln \frac{a_A'}{a_A}, \tag{25}$$

where a_A and a_A' represent the activities in the initial and final states respectively, and ΔF_A represents the increase in free energy accompanying the change.

Derivation of the Mass Law in Terms of Activities: Let us consider again the general reaction

$$aA + bB \cdots = cC + dD \cdots, \tag{26}$$

where A, B, C, and D may be either gases, dissolved substances, liquids or solids. The essential criterion that a condition of equilibrium exists in any process at constant temperature is that the free energy increase for the process shall be zero. For the reaction (26), at the condition of equilibrium, the sum

[1] See Chapter XII, and Lewis and Randall, Thermodynamics and Chemistry (McGraw-Hill Co., 1923).

of the molal free energies of A and B must be equal to the sum of the molal free energies of C and D; that is,

$$aF_A + bF_B \cdots = cF_C + dF_D \cdots. \tag{27}$$

Combining equations (24) and (27), we have, if we consider the activities of the reacting substances in the equilibrium mixture,

$$aRTlna_A + aC_A + bRTlna_B + bC_B \cdots = cRTlna_C + cC_C + dRTlna_D + dC_D \cdots \tag{28}$$

or

$$aC_A + bC_B - cC_C - dC_D \cdots = RTln \frac{a_C{}^c \times a_D{}^d \cdots}{a_A{}^a \times a_B{}^b \cdots}. \tag{29}$$

Since the quantities on the left hand side of the equation are constants fixed by the definition of the standard state, we may for any given temperature write equation (29)

$$K_a = \frac{a_C{}^c \times a_D{}^d \cdots}{a_A{}^a \times a_B{}^b \cdots}, \tag{30}$$

where K_a may be called the equilibrium constant in terms of the activities of the reacting constituents. This equation has been derived without any simplifying assumptions and may be regarded as perfectly general for any chemical reaction whatever.

It will be noted that equation (30) is quite similar to that originally proposed by Guldberg and Waage (4) except that the quite indefinite term "active mass" is replaced by the thermodynamically defined term "activity." In order to express equation (30) in terms of some experimentally measurable composition term, we must find a relation between the activity of each constituent and its partial pressure, mol. fraction, concentration, etc.

Fortunately, in many cases, relationships exist which enable us to derive approximate "mass laws" for practical application. Thus, for dilute gaseous systems, we have the activity approximately equal to the pressure, and by substituting in equation (30) $P = a$, we obtain

$$K_p = \frac{P_C{}^c \times P_D{}^d \cdots}{P_A{}^a \times P_B{}^b \cdots}, \tag{31}$$

which is evidently identical with equation (21) previously derived for gaseous systems. Since partial pressure (partial pressures should always be expressed in atmospheres), is defined by the relation $P_A = X_A P$, where X represents mol. fraction and P total pressure, we may also write

$$K_p = \frac{X_C{}^c \times X_D{}^d}{X_A{}^a \times X_B{}^b} \times P^{(c+d-a-b)} \cdots, \tag{32}$$

or, at any given pressure,

$$K_x = \frac{X_C{}^c \times X_D{}^d}{X_A{}^a \times X_B{}^b}, \tag{33}$$

where

$$K_x = K_p \times P^{(a+b-c-d)}. \tag{34}$$

Since for dilute gases we also have the relationship $PV = NRT$, and $\frac{N}{V} = C$, the concentration in mols. per liter, equation (30) may be written

$$K_p = \frac{C_C{}^c \times C_D{}^d \cdots}{C_A{}^a \times C_B{}^b \cdots} \times (RT)^{(c+d-a-b)},$$

whence

$$K_c = \frac{C_C{}^c \times C_D{}^d \cdots}{C_A{}^a \times C_B{}^b \cdots}, \tag{35}$$

where

$$K_c = K_p \times (RT)^{(a+b-c-d)}. \tag{36}$$

Combining equations (34) and (36), we obtain

$$K_c = K_x \cdot \left(\frac{RT}{P}\right)^{(a+b-c-d)} = K_x \cdot \left(\frac{V}{N}\right)^{(a+b-c-d)} \tag{37}$$

The numerical relationships between the three constants are given by equations (34), (36) and (37), from which it is clear that when $a + b = c + d$ the three constants are numerically equal. The selection of a particular equation in any given case depends frequently upon convenience in considering the data in question.

It should be noted that K_p and K_c are independent of the pressure, within the limits in which the gas laws are obeyed. At high pressures none of the equations may be expected to be exactly valid.

In applying equation (30) to equilibrium in homogeneous liquid systems, we find in general much greater difficulty in relating the activity of the constituents of an equilibrium mixture to their concentration than is true in the case of gases.

In the case of a "perfect solution," we may equate the activity at atmospheric pressure to the mol. fraction, and obtain an equation identical with equation (32), or

$$K_x = \frac{X_C{}^c \times X_D{}^d \cdots}{X_A{}^a \times X_B{}^b \cdots}. \tag{38}$$

Remembering that the concentration in mols. per liter is related to the mol. fraction by the equation

$$C = X \times \frac{N}{V}, \tag{39}$$

where V is the total volume and N the total number of mols. (including indifferent, or solvent, mols.) contained therein, we may write equation (38) as

$$K_x = \frac{C_C{}^c \times C_D{}^d \cdots}{C_A{}^a \times C_B{}^b \cdots} \times \left(\frac{V}{N}\right)^{(c+d-a-b)}. \tag{40}$$

If the number of indifferent mols., say of solvent, becomes quite large in comparison with the number of mols. of reacting constituents, neither V nor N will change greatly with changes in the concentrations of the reacting species and we may write, for a dilute solution,

$$K_c = \frac{C_C{}^c \times C_D{}^d \cdots}{C_A{}^a \times C_B{}^b \cdots}. \tag{41}$$

In aqueous solution, many data are at present available in the form of molalities, or mols. per 1000 grams of water. The molality is related to the concentration by the equation

$$M = C \cdot \frac{V}{k}, \tag{42}$$

where k is the number of kilograms of water contained in V liters of solution. Obviously, in dilute solutions, V/k approaches unity.

If we substitute molalities for concentrations in equation (41), we obtain

$$K_c = \frac{M_C{}^c \times M_D{}^d \cdots}{M_A{}^a \times M_B{}^b \cdots} \times \left(\frac{k}{V}\right)^{(c+d-a-b)} \tag{43}$$

or

$$K_m = \frac{M_C{}^c \times M_D{}^d \cdots}{M_A{}^a \times M_B{}^b \cdots}. \tag{44}$$

Equations (38), (41) and (44) are most frequently employed in the treatment of equilibrium in homogeneous liquid media.

The numerical relations existing between the constants K_x, K_c, and K_m, for equilibria in liquid media, are evidently

$$K_x = K_c \cdot \left(\frac{V}{N}\right)^{(c+d-a-b)}, \tag{45}$$

$$K_c = K_m \cdot \left(\frac{k}{V}\right)^{(c+d-a-b)}. \tag{46}$$

When $a + b = c + d$, the three constants are numerically identical, while K_c and K_m are very nearly identical for any dilute solution.

It is difficult to predict the extent to which equations (38), (41) and (44) may be expected to be valid in any given case. Many organic substances, particularly those similar in chemical constitution, generally approximate to the behavior of "perfect solutions" over a wide range of concentrations. On the other hand, solutions of highly ionized substances are so far from "perfect" that their behavior deserves special treatment (Chapters XI and XII). In general, the more nearly alike in composition substances entering into reaction may be, and the more dilute the solution in which they react, the more nearly the mol. fraction or molality is apt to measure the activity, and the more nearly the equilibrium laws of solutions are apt to be valid. The subject will be treated further in a later section.

We have gone into the various equilibrium constants in considerable detail, because considerable confusion sometimes results from the use of different "mass laws" without an understanding of the assumptions underlying their derivation, and of their relations to each other. All of the equations evidently express relations which represent a limiting condition which may be approximated under actual conditions.

In pages 424 to 426 we have derived a series of mass laws identical with those derived directly in pages 420 to 422, and actually involving identical assumptions concerning the behavior of the reacting constituents. The difference has been only one of method. Equations (33), (35), (37), (38), (41) and (44) were derived from the "universally valid" equation (30) by means of essentially the same simplifying assumptions that were employed in the preceding section.

It may be objected that when we speak of equation (30) as "universally valid" we are reasoning in a circle, as it is valid only because of the definition of the term "activity," and that since no simple general relation exists between the activity of a substance and its pressure or concentration, the equation has no real significance. In a sense this is certainly correct; nevertheless, there are important advantages in the use of the "activity" in the treatment of equilibrium.

If we do not utilize some such function, we can only derive various "mass laws" valid for limiting conditions, and in any actual case outside of these conditions we can only say that "the mass law does not hold." The use of an equation which is universally valid accomplishes several purposes. In the first place it emphasizes the limitations that are actually involved in all of the simpler mass laws, and these limitations are frequently overlooked; it furnishes a convenient basis for the investigation of equilibrium in cases in which the simple mass laws do not apply (particularly in such cases as involve highly ionized substances); and, in mathematical treatment involving the combination of different reactions, it furnishes an expression which may be combined with other similar expressions without involving assumptions which might be easily overlooked and which might complicate the mathematical treatment. Furthermore, the use of equation (30) emphasized the thermodynamic view that the condition of equilibrium is defined by the statement that the free energy increase at equilibrium must be equal to zero, and that any mass law is directly or indirectly an expression of this fact.

We shall therefore regard equation (30) as "the mass law," although we actually employ in most cases the simple equations derived therefrom.

The Increase in Free Energy Accompanying a Chemical Reaction

The increase in free energy accompanying a chemical reaction is an important thermodynamic function, which will be employed in later sections of this chapter in the derivations of relations expressing the variation of the equilibrium constant with the temperature and pressure. In order to calculate

the increase in free energy for any given chemical reaction, we must devise a mechanism by which, theoretically at least, the reaction can be caused to occur isothermally and reversibly.

The Free Energy Increase in a Reaction between Dilute Gases: Let us consider the reaction

$$aA + bB \cdots = cC + dD \cdots,$$

in which the reacting substances are dilute gases. Let the initial partial pressures of A and B be represented by P_A and P_B, and the final partial pressures of C and D by P_C and P_D.

We wish to carry out the reaction in a series of isothermal reversible steps. Let us imagine that a mols. of the substance A and b mols. of B, at partial pressures P_A and P_B, respectively, are contained in separate cylinders fitted with frictionless pistons, and provided with membranes, which can be opened when desired, permeable only to A and B, respectively.

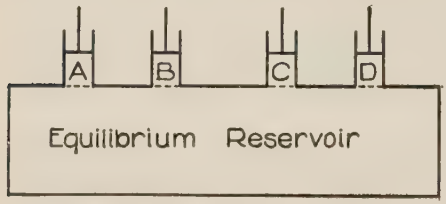

Fig. 1

Let us also imagine an indefinitely large reservoir containing A, B, C, and D in the proportions in which they exist in chemical equilibrium, their partial pressures being P_A', P_B', P_C', and P_D', respectively. The semi-permeable membranes of the cylinders of A and B open when desired into this reservoir. Similar membranes permeable only to C and D are open to cylinders which are to contain these substances. A diagram of the arrangement is given in Fig. 1.

Step 1.—Change the pressure of A, in the cylinder containing it, isothermally and reversibly from P_A to P_A', involving the increase in free energy, $a\int_{P_A}^{P_A'} VdP$. Change similarly the partial pressure of B from P_B to P_B', with the free energy increase, $b\int_{P_B}^{P_B'} VdP$.

Step 2.—Open the connections of the cylinders of A and B into the equilibrium reservoir, and introduce through the semi-permeable membranes a mols. of A and b mols. of B, at their partial pressures P_A' and P_B'.

Simultaneously withdraw from the reservoir c mols. of C and d mols. of D, at the partial pressures P_C' and P_D'. During this process the A and B introduced into the reservoir react to form C and D, thus keeping the composition of the reservoir only infinitesimally different from the equilibrium condition.

Since the partial pressures of A, B, C, and D in the cylinders were equal to the corresponding pressures in the reservoir, none of the processes occurring in Step 2 have involved any change in free energy.

Step 3.—Change, isothermally and reversibly, the partial pressures of C and D in the cylinders containing them, from P_C' to P_C and from P_D' to P_D,

respectively. This involves the free energy increases $c\int_{P_{C'}}^{P_C} VdP$ and $d\int_{P_{D'}}^{P_D} VdP$.

The net result of steps (1), (2), and (3) is the occurrence of the chemical reaction as required by the reaction equation and each step has been carried out isothermally and reversibly. The sum of the various free energy increases must be, therefore, the total free energy increase of the reaction, which is the quantity which we desired to derive. We may then write

$$\Delta F = a\int_{P_A}^{P_{A'}} VdP + b\int_{P_B}^{P_{B'}} VdP + c\int_{P_{C'}}^{P_C} VdP + d\int_{P_{D'}}^{P_D} VdP.$$

Now, if the gases are sufficiently dilute for the gas laws to be valid, we may write

$$\Delta F = aRTln\frac{P_{A'}}{P_A} + bRTln\frac{P_{B'}}{P_B} + cRTln\frac{P_C}{P_{C'}} + dRTln\frac{P_D}{P_{D'}} \tag{47}$$

or, rearranging,

$$\Delta F = RTln\frac{P_C{}^c \times P_D{}^d \cdots}{P_A{}^a \times P_B{}^b \cdots} - RTln\frac{P_{C'}{}^c \times P_{D'}{}^d \cdots}{P_{A'}{}^a \times P_{B'}{}^b \cdots}. \tag{48}$$

Recalling equation (31), equation (48) becomes

$$\Delta F = RTln\frac{P_C{}^c \times P_D{}^d}{P_A{}^a \times P_B{}^b} - RTlnK_p. \tag{49}$$

The free energy increase for a dilute gaseous reaction is evidently determined at constant temperature by the equilibrium constant, and by the initial and final partial pressures of the reacting species. If the latter should be each equal to unity, we have

$$\Delta F = -RTlnK_p. \tag{50}$$

The free energy increase for a reaction between perfect solutes in solution may be derived in an exactly similar way. However, it is preferable to consider the most general case, involving the activities of the reacting species.

Let us consider again the general reaction

$$aA + bB \cdots = cC + dD \cdots, \tag{51}$$

in which A, B, C, and D may be substances in any state whatever. Let a_A, a_B, etc., represent the activities of the reactants in the specified initial states, and a_C, a_D, etc., the activities of the resultants in the specified final states. The corresponding activities at the equilibrium state are a_A', a_B', a_C', and a_D'. We may imagine the reaction as being brought about by a mechanism similar to that outlined above for a gaseous system. Remembering that the free energy increase in changing a mol. of substance from activity a to activity a' is equal to $RTln(a'/a)$, and that the free energy increase at the condition of equilibrium is equal to zero, we may write for the free energy increase ac-

companying reaction (51)

$$\Delta F = RTln\frac{a_C{}^c \times a_D{}^d \cdots}{a_A{}^a \times a_B{}^b \cdots} - RTln\frac{a_C{}'^c \times a_D{}'^d \cdots}{a_A{}'^a \times a_B{}'^b \cdots}. \tag{52}$$

This may be written, remembering equation (30),

$$\Delta F = RTln\frac{a_C{}^c \times a_D{}^d}{a_A{}^a \times a_B{}^b} - RTlnK_a \tag{53}$$

or, for the reactions in which the initial activities of the reactants and the final activities of the resultants are each equal to unity, we have

$$\Delta F = -RTlnK_a. \tag{54}$$

The free energy increase represents an extremely useful function in considering the thermodynamics of chemical reactions. If we can determine the value of ΔF for a given reaction under given conditions, we can predict whether or not the reaction may occur spontaneously, since spontaneous change can occur only in the direction of a decrease in free energy. A negative value of ΔF, therefore, for a chemical reaction written in a given sense indicates that spontaneous reaction is possible in that sense; a positive value indicates that the reaction can occur only in the opposite sense. Furthermore we may employ equations (53) and (54) either to calculate ΔF when the equilibrium constant is known, or to calculate the equilibrium constant when ΔF is known. In addition to the relations expressed in equations (53) and (54), the free energy increase for a chemical reaction may be determined from the electromotive force of reversible cells (see Chapter XII), and through the third law of thermodynamics, from the entropies of the reacting substances (Chapter XVII). The calculation of free energy data by these different methods, and the combination of the data from all sources, has yielded so much valuable information that it is highly desirable that systematic determinations of the free energy changes of chemical reactions should be made, and the data expressed in unified form. In order to avoid confusion, it is necessary that unity of procedure should be followed in making the fundamental definitions of the quantities involved in the calculations. The most complete systematic calculations of free energy appear in the recent work by Lewis and Randall to which reference has already been made, and it seems advisable to adopt essentially their usage. They define the activity of a substance in such a way that for a pure chemical substance the activity is unity at atmospheric pressure, for that form of the substance stable under the prevailing conditions. For a solute, the activity is defined, for non-electrolytes, by the relation $a/x = 1$ when x approaches zero or as the solution approaches infinite dilution.

For solutions of electrolytes a special definition of activity is employed which is discussed in Chapter XII. The free energy increase of a chemical reaction, as calculated from the equilibrium constant by equation (54), refers to a change of state in which either pure solids, liquids and gases occur in the

equation, at atmospheric pressure, or in which dissolved substances are present in such concentration that their activity is equal to unity.

It should be emphasized that it is K_a which measures the free energy change, and not K_p, K_x or K_c unless the conditions are such that these equilibrium constants are equal to K_a. Thus, in order to calculate free energy change from equilibrium data, we must either make the measurements in solutions so dilute, or at gas pressures so low, that the activities of the reacting species are approximately given by their mol. fraction, partial pressures, etc.; or we must make measurements over a sufficient range of concentrations to permit extrapolation with reasonable certainty into the desired range of conditions. The calculation of free energy data and of equilibrium constants from free energy data will be treated briefly in a later section; for a complete discussion reference should be made to Lewis and Randall's Thermodynamics and Chemistry.

The Variation of Equilibrium Conditions with Temperature, Pressure, and Concentration

The Le Chatelier-Braun Principle: A state of equilibrium in a chemical reaction is determined by the temperature, the pressure, and the proportions of the substances present. We wish frequently to know, both qualitatively and quantitatively, the change in the condition of equilibrium which will be brought about by a change in one or more of the variable factors involved.

Qualitatively, these changes may be predicted by the use of the theorem of Le Chatelier-Braun, which may be stated as follows: If a change occurs in one of the factors determining a condition of equilibrium, the equilibrium shifts in such a way as to tend to annul the effect of the change. From this statement it follows that the effect of an increase in temperature, all other factors remaining constant, is to shift an equilibrium in the direction in which *absorption of heat* occurs, as this change would tend to annul the effect of the heat added in changing the temperature; the effect of an increase in pressure will be to shift the equilibrium in the direction in which a *decrease in volume* occurs, as this change would tend to annul the effect of the increased pressure; an increase in the concentration of one of the substances present at equilibrium will shift the equilibrium in such a way as to tend to decrease the concentration of that substance. This principle is an extremely useful one, and serves not only for purely qualitative predictions, but also as a check upon the quantitative results in which errors of calculation may appear.

The quantitative information is, of course, usually more important and will be treated at length below, but it is instructive to consider the results of every quantitative calculation in the light of the Le Chatelier-Braun principle.

The Effect of Temperature upon Chemical Equilibrium: The combination of the first and second laws of thermodynamics gives us for a reversible change the Gibbs-Helmholz equation (Chap. II)

$$\Delta A - \Delta U = T\left(\frac{d(\Delta A)}{dT}\right)_v. \tag{55}$$

In this equation it is assumed that the initial and final volumes are not functions of the temperature. Since in most chemical reactions pressure rather than volume is fixed by the conditions assumed for the reaction, it is preferable to write equation (55) in terms of the free energy increase and the increase in heat content, so that it becomes

$$\Delta F - \Delta H = T\left(\frac{d(\Delta F)}{dT}\right)_p. \tag{56}$$

Equation (53) gives us, for any reaction at constant temperature,

$$\Delta F = RTln\frac{a_C{}^c \times a_D{}^d \cdots}{a_A{}^a \times a_B{}^b \cdots} - RTlnK_a, \tag{57}$$

where K_a is the equilibrium constant and a_A, etc., represent the activities of the reacting constituents in the specified initial and final states.

Combining (56) and (57), and rearranging, we obtain

$$\frac{d(\Delta F)}{dT} = -\frac{\Delta H}{T} - RlnK_a + Rln\frac{a_C{}^c \times a_D{}^d \cdots}{a_A{}^a \times a_B{}^b \cdots}. \tag{58}$$

Differentiating (57) with respect to T and remembering that since the values of a are arbitrarily chosen and not determined by temperatures, the expression

$$RTdln\left(\frac{a_C{}^c \times a_D{}^d \cdots}{a_A{}^a \times a_B{}^b \cdots}\right)\Big/ dT$$

is equal to zero, we have

$$\frac{d(\Delta F)}{dT} = -RlnK_a - RT\frac{dlnK_a}{dT} + Rln\frac{a_C{}^c \times a_D{}^d \cdots}{a_A{}^a \times a_B{}^b \cdots}. \tag{59}$$

Equating the right hand members of (58) and (59) and simplifying, we have

$$\frac{dlnK_a}{dT} = \frac{\Delta H}{RT^2}. \tag{60}$$

This important equation, usually called the equation of van't Hoff, expresses quantitatively the change of the general "mass law" equilibrium constant with the temperature, as a function of ΔH, which is equal to $-Q_p$, where Q_p is the heat evolved by the reaction at constant pressure. Under conditions in which the special mass laws (equations (31), (33) and (38), (41), (44)) may be expected to be valid, equation (60) may be modified by combining it with the relation between K_a and the equilibrium constant in question.

Thus, under conditions in which $P = a$, we have

$$\frac{dlnK_p}{dT} = -\frac{Q_p}{RT^2}. \tag{61}$$

Since $K_p = K_c(RT)^{-n}$, where $n = a + b - c - d$ (equation (36)), we may write

$$lnK_p = lnK_c - nlnRT \tag{62}$$

and, combining with (61),

$$\frac{dlnK_c}{dT} - \frac{ndlnRT}{dT} = -\frac{Q_p}{RT^2} \tag{63}$$

or

$$\frac{dlnK_c}{dT} = -\frac{Q_p}{RT^2} + \frac{n}{T} = -\frac{Q_p - nRT}{RT^2} = -\frac{Q_v}{RT^2}. \tag{64}$$

Similarly, making use of equation (34),

$$K_p = K_x \cdot P^{-n} \tag{65}$$

and

$$\frac{dlnK_x}{dT} - \frac{dlnP^n}{dT} = -\frac{Q_p}{RT^2}. \tag{66}$$

For reactions at constant pressure, P, therefore, equation (66) becomes

$$\frac{dlnK_x}{dT} = -\frac{Q_p}{RT^2}. \tag{67}$$

Equation (60) may be integrated if ΔH is independent of temperature or may be represented as a function of temperature. In the first case we obtain

$$lnK_a = -\frac{\Delta H}{RT} + C, \tag{68}$$

or, between T_1 and T_2,

$$lnK_{1_a} - lnK_{2_a} = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \tag{69}$$

Changing to ordinary logarithms and inserting the numerical value of R, equation (69) becomes

$$log\ K_1 - log\ K_2 = -\frac{\Delta H}{4.5787}\left(\frac{1}{T_1} - \frac{1}{T_2}\right). \tag{70}$$

This equation is widely used for the calculation of the effect of temperature upon equilibrium in cases where the heat of reaction is known, and for the calculation of the heat of reaction where the equilibrium constant is known at more than one temperature. Even if ΔH is really dependent upon temperature, equation (70) usually gives approximately correct results if the interval between T_1 and T_2 is not too great.

In general, the variation of ΔH with T is given by the Kirchoff formula (Chap. II),

$$\frac{d(\Delta H)}{dT} = \Delta C_p, \tag{71}$$

where ΔC_p represents the difference between the heat capacities of the substances on the right hand side of the equation for the chemical reaction and those of the left. It is frequently possible to express the heat capacities of each substance as a series function of temperature, of the form

$$C_p = m + nT + oT^2 \cdots. \tag{72}$$

In this case, considering again the reaction

$$aA + bB \cdots = cC + dD \cdots, \tag{73}$$

we have

$$\Delta C_p = (cm_C + dm_D - am_A - bm_B) + (cn_C + dn_D - an_A - bn_B)T + (co_C + do_D - ao_A - bo_B)T^2 \cdots \tag{74}$$

or,

$$\Delta C_p = q + rT + sT^2 \cdots, \tag{75}$$

where q, r and s represent the terms in the parentheses, and are numerical constants for any given reaction.

Combining (71) and (75), we obtain

$$\frac{d(\Delta H)}{dT} = (q + rT + sT^2 \cdots) \tag{76}$$

and, integrating,

$$\Delta H = \Delta H_0 + qT + \tfrac{1}{2}rT^2 + \tfrac{1}{3}sT^3 \cdots. \tag{77}$$

The integration constant is called ΔH_0, since it is the value which ΔH reaches in equation (77) if T is made equal to zero.

If we combine equations (77) and (60), we obtain

$$\frac{dlnK_a}{dT} = \frac{\Delta H_0}{RT^2} + \frac{q}{RT} + \frac{1}{2}\frac{r}{R} + \frac{1}{3}\frac{s}{R}T \cdots \tag{78}$$

or

$$lnK_a = -\frac{\Delta H_0}{RT} + \frac{q}{R}lnT + \frac{1}{2}\frac{r}{R}T + \frac{1}{6}\frac{s}{R}T^2 \cdots + C. \tag{79}$$

Equation (79) expresses accurately the effect of temperature upon chemical equilibrium, and should always be employed in making calculations over a wide temperature interval, provided the necessary data concerning the heat capacities of the reacting substances are available.

If we combine equation (79) with equation (54), we obtain

$$\Delta F = \Delta H_0 - qTlnT - \tfrac{1}{2}rT^2 - \tfrac{1}{6}sT^3 \cdots - C'T, \tag{80}$$

which expresses the change of the "standard" free energy increase of a reaction with change in temperature. This equation is an extremely important one in the systematic calculation of free energy data.

Very frequently accurate data concerning the heat capacities of the reacting substances over a wide range of temperature are not available, but values of the equilibrium constant at a number of temperatures are available. In this case it is often possible to express the variation of the equilibrium constant with the temperature by means of empirical formulæ, usually corresponding in type to equation (79), and differing only in the numerical values of the constants. Several different equations may express given numerical data over certain temperature ranges almost equally well, and may serve for the practical calculation of the equilibrium constant at temperatures differing from those measured. It is desirable, however, to utilize in all calculations equation (79), containing actual specific heat data, wherever these are available. Specific examples of these formulæ, both of the empirical type and those employing exact specific heat data, will be given in a later section.

The Effect of Pressure upon Chemical Equilibrium: Quantitatively the effect of pressure upon chemical equilibrium may be followed by considering the various equilibrium constants. The equilibrium constant, K_p, is, as we we have seen, related, in dilute gaseous systems, to the free energy and partial pressures of the constituents of a reaction system by the equation

$$\Delta F = RT\, ln \frac{P_C{}^c \times P_D{}^d}{P_A{}^a \times P_B{}^b} - RT\, ln\, K_p. \tag{49}$$

This expression was derived with the aid of an equilibrium box in which the constituents of the reaction system were in equilibrium. No restrictions were placed on this box other than that the constituents were dilute enough to obey the gas laws and that they were in equilibrium. Hence, since the free energy is dependent only on the initial and final states of the system and is independent of the path between (i.e., the equilibrium box) it follows that K_p must be a constant at constant temperature independent of the magnitudes of the individual partial pressures and of the total pressure in the equilibrium box. That is to say, $dK_p/dP = dlnK_p/dP = 0$; the equilibrium constant, K_p, is independent of the total pressure, provided the gas laws are obeyed. When this latter is not true the same process of reasoning leads to the conclusion that K_a, the activity constant correcting for deviations from the gas laws, is constant, independent of pressure.

Similarly, K_c, which is related to K_p by a factor not dependent on pressure (Equation 36) is also independent of pressure. The numerical value of the equilibrium constant, K_x, however, varies with the pressure. Writing from equation 34,

$$K_x = K_p \times P^{(a+b-c-d)} \tag{81}$$

and taking logarithms, we have

$$ln\, K_x = ln\, K_p + (a + b - c - d)\, ln\, P. \tag{82}$$

Differentiating with respect to P, we obtain

$$\frac{dlnK_x}{dP} = \frac{(a + b - c - d)}{P}. \tag{83}$$

When $PV = RT$, this expression becomes

$$\frac{d\ln K_x}{dP} = \frac{(a + b - c - d)V}{RT}. \tag{84}$$

It is apparent that if $a + b = c + d$, K_x also is independent of P.

The quantitative effect of a change in pressure upon the proportions of the reacting constituents present at equilibrium may be calculated very simply for a dilute gaseous reaction.

We may write equation (31) in the form

$$K_p = \frac{N_C{}^c \times N_D{}^d}{N_A{}^a \times N_B{}^b} \times \frac{P^{(c+d-a-b)}}{N^{(c+d-a-b)}}, \tag{85}$$

where N represents the total number of mols. in the system. Since K_p is constant, it is clear that when $a + b = c + d$ the second (P/N) factor of the right hand side of the equation becomes unity, and no change whatever takes place in the relative number of mols. of the reacting constituents with a change in pressure. If, however, $a + b$ is not equal to $c + d$, the P/N factor will differ from unity and a change must occur in the first factor, by reaction between the constituents, in order to satisfy the equation.

Let us consider a system at equilibrium at pressure P_1, for which the numerical values of N_C, N_D, N_A, N_B, etc., have been determined. Let us now change the pressure to P_2. Let x represent the decrease (which might actually be an increase) in the number of mols. of A after equilibrium has been re-established.

Substituting the new values in equation (85), we have

$$K_p = \frac{\left(N_C + \frac{cx}{a}\right)^c \left(N_D + \frac{dx}{a}\right)^d \cdots}{(N_A - x)^a \left(N_B - \frac{bx}{a}\right)^b \cdots} \times \frac{P_2{}^{(c+d-a-b)}}{\left(N_1 - \frac{(c + d - a - b)x}{a}\right)^{(c+d-a-b)}}. \tag{86}$$

Since all of the quantities in the equation except x are known, the value of x, and hence the extent of the shift of equilibrium, may be readily calculated.

The effect of pressure upon equilibrium in the liquid phase is ordinarily negligible for moderate changes in pressure. For very considerable pressure changes, however, it may become quite appreciable. The magnitude of the effect, in the case of a perfect solution, may be shown from the following consideration.

If the reaction

$$aA + bB \cdots = cC + dD \cdots \tag{87}$$

occurs at unit pressure P_1, the free energy increase is given by the equation (compare equation (53))

$$\Delta F_1 = cF_{1_C} + dF_{1_D} - aF_{1_A} - bF_{1_B} = RTln\frac{a_C{}^c \times a_D{}^d \cdots}{a_A{}^a \times a_B{}^b \cdots} - RTlnK_a. \quad (88)$$

Since at unit pressure the activity of a perfect solution is equal to its mol. fraction, we may write $a = x$, and equation (88) becomes

$$\Delta F_1 = RTln\frac{X_{1_C}{}^c \times X_{1_D}{}^d \cdots}{X_{1_A}{}^a \times X_{1_B}{}^b \cdots} - RTlnK_{1_x}. \quad (89)$$

If instead of carrying out the reaction at pressure P_1 we raise the pressure to P_2, the molal free energies of each constituent will be increased according to the equation (Chap. II)

$$F_2 = F_1 + \int_{P_1}^{P_2} VdP. \quad (90)$$

The free energy increase of the reaction at pressure P_2 is given, therefore, by the equation

$$\begin{aligned}\Delta F_2 = &- aF_{1_A} - bF_{1_B} + cF_{1_C} + dF_{1_D} - a\int_{P_1}^{P_2} V_A dP \\ &- b\int_{P_1}^{P_2} V_B dP + c\int_{P_1}^{P_2} V_C dP + d\int_{P_1}^{P_2} V_D dP.\end{aligned} \quad (91)$$

Combining (89) and (91), we have

$$\begin{aligned}\Delta F_2 = &- RTlnK_{1_x} + RTln\frac{X_{1_C}{}^c \times X_{1_D}{}^d}{X_{1_A}{}^a \times X_{1_B}{}^b} - a\int_{P_1}^{P_2} V_A dP \\ &- b\int_{P_1}^{P_2} V_B dP + c\int_{P_1}^{P_2} V_C dP + d\int_{P_1}^{P_2} V_D dP.\end{aligned} \quad (92)$$

Now the free energy increase, ΔF_2, can also be determined by carrying out the reaction through an isothermal reversible process at pressure P_2, similar to that used in deriving equation (53). Each reactant is first changed from its initial mol. fraction (which is still X_1) to the equilibrium value X_2, involving the free energy increase per mol. of $RTln\frac{X_2}{X_1}$, and is then caused to react at the equilibrium condition. The total free energy increase involved in the process is given (equation (53)) by the equation

$$\Delta F_2 = RTln\frac{X_{1_C}{}^c \times X_{1_D}{}^d \cdots}{X_{1_A}{}^a \times X_{1_B}{}^b \cdots} - RTln\frac{X_{2_C}{}^c \times X_{2_D}{}^d \cdots}{X_{2_A}{}^a \times X_{2_B}{}^b \cdots}, \quad (93)$$

where the second member of the right hand side of the equation is evidently K_{2_x}. Equating (92) and (93), we have

$$RTlnK_{2_x} - RTlnK_{1_x} = a\int_{P_1}^{P_2} V_A dP + b\int_{P_1}^{P_2} V_B dP - c\int_{P_1}^{P_2} V_C dP - d\int_{P_1}^{P_2} V_D dP. \tag{94}$$

If $P_2 - P_1 = dP$, that is, for an infinitesimal change, we may write

$$\frac{dlnK_x}{dP} = \frac{aV_A + bV_B - cV_C - dV_D}{RT}. \tag{95}$$

This equation was first derived by Planck[1] and shows that the rate of change of the equilibrium constant, K_x, with the pressure, is equal to the decrease in the sum of the molal volumes of the reacting substances, divided by RT.

If this equation is compared with that previously derived for a gaseous equilibrium, equation (84), it is apparent that the two become identical when the molal volumes of the constituents are equal to each other, as would be true for dilute gases.

If we consider the relation between K_x and K_c, the mass law constants in terms of the molal concentrations, we may derive an expression for the rate of change of K_c with the pressure.

Thus, from equation (45),

$$K_c = K_x\left(\frac{V}{N}\right)^{(a+b-c-d)}, \tag{96}$$

where N is the total number of mols. (of all kinds) and V the total volume. Taking logarithms,

$$lnK_c = lnK_x + (a + b - c - d)ln\frac{V}{N}. \tag{97}$$

Differentiating, we obtain

$$\frac{dlnK_c}{dP} = \frac{dlnK_x}{dP} + (a + b - c - d)\frac{dln\left(\frac{V}{N}\right)}{dP}. \tag{98}$$

If the solution is dilute, we may replace $\frac{V}{N}$ by $\overline{V}$, the molal volume of the solvent, and obtain, using equation (95),

$$\frac{dlnK_c}{dP} = \frac{aV_A + bV_B - cV_C - dV_D}{RT} + (a + b - c - d)\frac{1}{\overline{V}}\frac{d\overline{V}}{dP}. \tag{99}$$

The increase in the partial molal free energy of the solvent with the pressure is given by the equation

$$d\overline{F} = \overline{V}dP. \tag{100}$$

[1] Thermodynamics, English Translation, p. 232 (1903), Longmans, Green and Co.

Now, in the chemical reaction in question the increase in the partial molal free energy of the solvent is also given by the equation

$$\bar{dF} = RTln\frac{X_2}{X_1}, \tag{101}$$

where X_1 and X_2 are the mol. fractions of *solvent* before and after the change; i.e.,

$$X_1 = \frac{N - a - b}{N} \quad \text{and} \quad X_2 = \frac{N - c - d}{N}.$$

If the solution is quite dilute, $a + b$ and $c + d$ are small as compared with N, and, expanding equation (101) by McLaurin's theorem and neglecting higher powers, we obtain

$$\bar{dF} = RT\frac{(a + b - c - d)}{N}. \tag{102}$$

Combining equations (102) and (100),

$$\bar{V} = \frac{RT(a + b - c - d)}{NdP}. \tag{103}$$

Substituting this value for $\bar{V}$ in equation (99), we obtain

$$\frac{dlnK_c}{dP} = \frac{aV_A + bV_B - cV_C - dV_D}{RT} + \frac{Nd\bar{V}}{RT}, \tag{104}$$

or, since $(aV_A + bV_B - cV_C - dV_D + Nd\bar{V})$ is equal to the total decrease in volume, $-\Delta V$, which occurs when the reaction takes place,

$$\frac{dlnK_c}{dP} = -\frac{\Delta V}{RT}. \tag{105}$$

This equation has been recently obtained by Rice[1] and by Williams,[2] employing a cyclic process involving the osmotic work produced by concentration changes.

The equation has been tested experimentally by Fanjung,[3] who measured the dissociation of weak organic acids at high pressures.

The Effect of Dilution at Constant Pressure: The effect of volume change upon a chemical equilibrium is more readily seen if we rearrange somewhat the fundamental mass law expressions. Thus we may write equation (31)

$$K_p = \frac{N_C{}^c \times N_D{}^d}{N_A{}^a \times N_B{}^b} \times \frac{P^{(c+d-a-b)}}{(N_A + N_B + N_C + N_D)^{(c+d-a-b)}} \tag{106}$$

and equation (35)

$$K_c = \frac{N_C{}^c \times N_D{}^d}{N_A{}^a \times N_B{}^b} \times V^{(a+b-c-d)}. \tag{107}$$

[1] *Trans. Farad. Soc.*, **12**, 318 (1917).
[2] *Trans. Farad. Soc.*, **16**, 458 (1921).
[3] *Z. physik. Chem.*, **14**, 673 (1894).

The effect of dilution of the equilibrium system at constant pressure may now be considered. If the diluent is a substance which does not participate in the chemical reaction, its effect, in general, is only to increase the total number of molecules ($N_A + N_B + N_C + N_D + \cdots$), and hence the volume. If $a + b = c + d$, it is obvious that the equilibrium is unchanged by such addition, because in such cases the "total number of molecules" factor and the volume factor become unity. If $(a + b)$ is greater than $(c + d)$, the equilibrium must shift with increasing volume in the direction expressed by the equation for the reaction, from left to right, until the new values of N_A, N_B, etc., satisfy equations (106) and (107). If $(a + b)$ is less than $(c + d)$, the reverse change must occur.

If the dilution is made with one of the reacting constituents, at constant pressure, the effect on the reaction is not so simply predictable, qualitatively, but is always calculable quantitatively from equation (106) and (107) when the values of N_A, N_B, etc., are known for the particular case.

In this connection it is of interest to consider the proportions in which the reactants for any given reaction should be employed in order to give, at equilibrium, a maximum yield of resultants.

Let us write the reaction

$$aA + bB + cC \cdots = dD + eE + fF \cdots. \tag{108}$$

Let X be the mol. fraction of D present at equilibrium. Then, if no D, E, or F was present at the beginning of the reaction, we have

$$\frac{eX}{d} = \text{the mol. fraction of } E \text{ at equilibrium,}$$

$$\frac{fX}{d} = \text{the mol. fraction of } F \text{ at equilibrium.}$$

Let $r_B, r_C \cdots$ represent the ratio of the mol. fractions of B, C, etc., at equilibrium to the mol. fraction of A. Since the sum of the mol. fractions must be unity, we have

$$X_A + r_B X_A + r_C X_A \cdots + X\left(\frac{d + e + f}{d}\right) = 1. \tag{109}$$

If we denote the term $\left(\frac{d + e + f}{d}\right)$ by m, we have for the various mol. fractions

$$X_A = \frac{1 - mX}{1 + r_B + r_C \cdots},$$

$$X_B = \frac{r_B(1 - mX)}{1 + r_B + r_C \cdots},$$

$$X_C = \frac{r_C(1 - mX)}{1 + r_B + r_C \cdots}.$$

Writing the equation for the mass law at constant temperature and pressure, and substituting the values given above, we have

$$K_x = \frac{X^d \times \left(\frac{eX}{d}\right)^e \times \left(\frac{fX}{d}\right)^f \cdots}{\left(\frac{1 - mX}{1 + r_B + r_C \cdots}\right)^a \times \left(\frac{r_B(1 - mX)}{1 + r_B + r_C \cdots}\right)^b \times \left(\frac{r_C(1 - mX)}{1 + r_B + r_C \cdots}\right)^c \cdots} \tag{110}$$

or, simplifying,

$$K_x = \frac{X^{(d+e+f)} \dfrac{d^d \times e^e \times f^f}{d^{(d+e+f\ldots)}}}{\left(\frac{1 - mX}{1 + r_B + r_C}\right)^{(a+b+c)} \times r_B{}^b \times r_C{}^c} \cdot \tag{111}$$

If we denote the two constant factors in the numerator by l and n, we have

$$\frac{nX^l}{(1 - mX)^{(a+b+c)}} = K_x \frac{r_B{}^b \times r_C{}^c \cdots}{(1 + r_B + r_C \cdots)^{(a+b+c\ldots)}} \cdot \tag{112}$$

By applying the principles of the differential calculus, it may be shown that X is a maximum when $r_B = \frac{b}{a}$; $r_C = \frac{c}{a}$; or when

$$\frac{X_A}{a} = \frac{X_B}{b} = \frac{X_C}{c} \cdots.$$

This can, however, only be the case when the same proportions held in the original mixture or, in other words, when the original mixture contained the reactants in the proportions which are required by the chemical equation. As an illustration, in the reaction

$$N_2 + 3H_2 = 2NH_3,$$

the maximum percentage of NH_3 that can be in equilibrium with a mixture of N_2 and H_2 at any given pressure and temperature is produced by bringing to equilibrium a mixture of N_2 and H_2 in the molal ratio of 1 : 3.

The effect of the addition to the equilibrium mixture of indifferent or reacting substances at constant volume is clear from consideration of equation (107). Thus, an indifferent substance will not be expected to change in any way an equilibrium at constant volume (except as indicated below), and the effect of an addition of one of the reacting constituents will be to displace the equilibrium in such a way as to decrease the number of mols. of the other constituents on the side of the chemical equation which includes the substance added, and to increase the number of mols. of the substances on the opposite side of the equation.

In considering the effect upon a system in equilibrium, we have considered the addition of substances not participating in the reaction as merely increasing the total number of molecules. This assumes, however, that the activities of the reacting species are still equal to their mol. fractions or to their partial pressures. If the added substance affects this relationship, it will be expected to have a specific influence on the equilibrium concentrations. For dilute gases in general, the addition of an indifferent gas does not affect the other gases measurably, but with gases at high pressures, and in the case of liquid solutions, the effect of adding "indifferent" substances may not be predicted simply from the volume change. With many organic compounds, the activity may be approximately given by the mol. fraction over a wide range of concentrations, but, in the case of other substances, particularly strong electrolytes, the activities of the reacting species may be markedly affected by the addition of apparently indifferent substances, and the equilibrium concentrations may change accordingly.

The special case involving the addition of a catalyst is discussed further below and the effect of a solvent in liquid systems will be treated in a later section.

Catalysts and Equilibrium: In the experimental measurement of equilibrium it very frequently happens that the rate of the reaction is not sufficient to bring about the condition of equilibrium in a reasonable time at the temperature at which it is desired to operate. In such cases it is usual to resort to the use of various substances which accelerate the *rate* of the reaction without apparently affecting the equilibrium. As the literature contains frequent statements that "a catalyst cannot affect the equilibrium" and occasional objections to this view, it may be well to consider the subject in some detail.

The general law of mass action, equation (30), was derived from consideration of the initial and final states of the system, and must be independent of the mechanism by which the change takes place. It follows, therefore, that the activity constant, K_a, and the free energy change for the reaction must be unaffected by the presence of any substance occurring on both sides of the chemical equation, provided the equation is otherwise unchanged. Thus, if a mixture of nitrogen and hydrogen is passed over a solid catalyst so slowly that equilibrium is obtained, the partial pressure of N_2, H_2 and NH_3 in the issuing gas will be necessarily the same as those which would have been present had the equilibrium been produced in the absence of a catalyst. In all cases of this type it is quite clear that the catalyst does not affect the equilibrium. Nevertheless it is quite possible for a catalyst to affect the equilibrium *concentrations* for a given reaction, if it is present in such quantity as to affect the activity of one or more of the reacting species. Thus, strong mineral acids are known to accelerate the reaction between alcohols and organic acids, and also the hydrolysis of the corresponding esters, and acids have been used as catalysts to facilitate the measurement of equilibrium in such reactions. The mol. fractions of ester, alcohol, acid and water may, however, have in such cases appreciably different values from those obtained without the use

of a catalyst, for the mineral acid affects the *activity of the water* (and probably, to a lesser extent, the other constituents), so that the activity of the water is no longer equal to its mol. fraction. This effect is particularly apt to occur in equilibria which involve electrolytes, either as reactants or as catalysts, and must be taken into consideration in measurements of equilibrium.

Thus, in measurements in which the catalyst is actually present in the system when the equilibrium is measured, the possibility must be considered that it may have an effect upon the activity of the reacting species, and thus lead to erroneous values for the equilibrium constant and the free energy change. This is, of course, also true of any "indifferent" molecular species which may be present in the system, as indicated above.

The difficulties which have arisen in considering the effect or lack of effect of a catalyst upon equilibrium have usually arisen from failure to consider carefully the assumptions underlying the particular equilibrium expressions which may have been employed.

In general, there is no serious difficulty in determining experimentally the question of the possible influence of the catalyst upon the equilibrium.

Measurement of Chemical Equilibrium

The experimental measurement of chemical equilibrium frequently presents problems of considerable difficulty. The position of equilibrium may be such that the reaction goes nearly to completion in one direction, and the concentrations of one or more of the reacting species may become immeasurably small. In other cases, the rate of the reaction may be so slow that equilibrium is not established in any convenient time at the temperature at which it is desired to measure it. Again, the rate of reaction may be so rapid that an attempt to analyze the equilibrium mixture results in a shift of the equilibrium. In the reactions of organic chemistry, and in many inorganic reactions, the problem is complicated by the occurrence of other reactions than the one whose equilibrium it is desired to measure. No general procedure can be indicated for the determination of the condition of equilibrium, as each problem is apt to require individual treatment; a few types of experimental method which have been used successfully may, however, be noted. The first step, in general, consists in determining that the reaction proceeds in each direction at some definite temperature, at a rate sufficiently rapid to permit the establishment of equilibrium within a reasonable time. The rate at a given temperature may frequently be increased by the selection of a suitable catalyst, which should not affect the equilibrium (see, however, the preceding section). Known proportions of the reacting substances are then brought in contact and are kept at the temperature in question until the mixture does not change in composition with increased time.

The analysis of the mixture must then be carried out in such a way as to prevent appreciable change in the composition by reaction during the time necessary for the analysis. Similar determinations should be made in which the equilibrium is approached from the opposite side, and experiments in which

the initial proportions of reactants are varied are usually necessary in order to calculate definitely an equilibrium "constant" for the reaction.

If possible, the analysis of the mixture is made at the temperature of the measurement of the equilibrium, by the determination of some physical property whose change can be shown to be proportional to the extent of reaction. Thus, the density may measure the extent of a reaction between gases in which the total number of molecules changes with the reaction; color, refractive index, optical rotation, etc., may in individual cases serve to measure the equilibrium concentrations.

If the analysis cannot be made without disturbing the system, recourse may be had to the procedure of lowering the temperature of the mixture very rapidly to some temperature so low that the rate of reaction is inappreciable in the time necessary for an analysis. The feasibility of this process will vary with the individual case.

In the case of reactions between gases, which will often occur with considerable velocity only at the surface of solid catalysts, dynamic methods are frequently employed, the reacting mixture being passed over the catalyst so slowly that further decrease in the rate of flow does not produce further change in composition (thus indicating the existence of equilibrium), and the gas issuing from the catalyst is cooled and analyzed. Since the rate of the reaction in the absence of the catalyst is frequently negligible, it is thus possible to maintain the mixture unchanged from the equilibrium condition for considerable periods of time.

In a great many cases in which it has not been found possible to measure the equilibrium of a chemical reaction directly because of experimental difficulties, it becomes possible to calculate it indirectly from a determination of the equilibria for reactions which, when combined, will give the reaction in question. Thus, consider the reactions

$$H_2 + \tfrac{1}{2}O_2 = H_2O, \tag{113}$$

$$CO + \tfrac{1}{2}O_2 = CO_2, \tag{114}$$

$$CO + H_2O = CO_2 + H_2, \tag{115}$$

for which at high temperatures and moderate pressures we may write

$$K_p' = \frac{P_{H_2O}}{P_{H_2} \times P_{O_2}^{1/2}}, \tag{116}$$

$$K_p'' = \frac{P_{CO_2}}{P_{CO} \times P_{O_2}^{1/2}}, \tag{117}$$

$$K_p''' = \frac{P_{CO_2} \times P_{H_2}}{P_{CO} \times P_{H_2O}}. \tag{118}$$

Each of these equations represents the relation which must exist at equilibrium between the partial pressures of the reacting constituents, regardless of any other substances which may be present. In a system at equilibrium containing both H_2O and CO_2, CO, H_2 and O_2 must also be present, and the partial pressures of the different constituents must adjust themselves in such a way that all three equations are satisfied. Obviously, then, equations (116), (117) and (118) are properly to be regarded as simultaneous equations, and if any two are known the third may be calculated. Thus, it might be that the dissociation of water could not be measured at a given temperature; while that of CO_2 (117) and the equilibrium of the water gas reaction (118) were experimentally measurable. The dissociation constant for H_2O is then calculable without direct measurement.

This principle is of the utmost importance, and its use has permitted the calculation of the equilibrium of numerous important reactions.

Furthermore, the equilibrium constant is directly related to the free energy of reaction (p. 305) which is frequently calculable from such data as the electromotive force of cells (Chap. XII) or from the entropies of the reacting and resulting substances (Chap. XVII). It has sometimes been possible to utilize very elaborate combinations of reactions to calculate the equilibrium constant not directly measurable.[1] It must be remembered, however, that cumulative experimental error is apt to occur if too many different data are combined.

If the approximate condition of equilibrium is known, it is frequently possible to determine the exact condition by preparing a series of mixtures approximating in composition that estimated for the equilibrium, and noting their rate of change, by means of analysis, or by some physical measurement. If it can be shown that one mixture is changing in one direction, and another in the opposite direction, the true equilibrium must lie between these limits, and by repeating the experiments it is possible to make the limits as narrow as is desired. This procedure is frequently employed when complicating reactions are apt to occur if too long a period of time were allowed for the reaction.

Homogeneous Equilibrium in the Gaseous Phase

Most measurements of gaseous equilibrium have been carried out at pressures in the neighborhood of atmospheric, and at somewhat elevated temperatures, so that the activity of each reacting species is approximately equal to its partial pressure. Under these conditions the equilibrium is expressed by equation (31) above.

Reactions in which no Change in the Number of Molecules Occur: If the number of molecules of resultants is equal to that of the reactants, it is apparent from equation (31) that changes in the *total pressure* of the system will be without effect upon the position of equilibrium, so long as the partial pressures of the reacting substances may be considered as approximately equal to their activities. Examples of this type of reaction which have been the

[1] See Lewis and Randall, Thermodynamics and Chemistry, 488, 528, 1923.

subject of extensive experimental investigation are

$$H_2 + I_2 = 2HI \tag{119}$$

and

$$H_2 + CO_2 = CO + H_2O. \tag{120}$$

The former of these reactions was investigated thoroughly by Bodenstein,[1] who allowed known quantities of hydrogen and iodine to react until equilibrium was reached, and then, after sudden cooling, determined the hydriodic acid formed.

If a represents the number of mols. of H_2 taken at the start of the reaction, b the number of mols. of I_2, $2x$ the number of mols. of HI formed after equilibrium has been reached, and P the total pressure, we have, for the equilibrium partial pressures,

$$P_H = \frac{(a - x)P}{a + b},$$

$$P_{I_2} = \frac{(b - x)P}{a + b},$$

$$P_{HI} = \frac{(2x)P}{a + b},$$

whence

$$K_p = \frac{P_{HI}^2}{P_{H_2} \times P_{I_2}} = \frac{4x^2}{(a - x)(b - x)}. \tag{121}$$

In Table I are given characteristic experimental data obtained by Bodenstein, and also values of x calculated from equation (121), taking the value of K as 50.4, the mean experimental value at 454°. The close agreement shows that equation (121) represents quite closely the experimental facts of this equilibrium.

TABLE I

EQUILIBRIUM DATA, $H_2 + I_2 = 2HI$
Temperature = 454°; $K_p = 50.4$

H_2 at Start cc. (a)	I_2 at Start cc. (b)	HI Formed cc. ($2x$)	HI Calc. from Eq. (121) ($2x$)
8.10	2.94	5.64	5.66
7.94	5.30	9.49	9.52
8.07	9.27	13.47	13.34
8.12	14.44	14.93	14.82
8.02	27.53	15.54	15.40
7.89	33.10	15.40	15.12

[1] *Z. phy ik. Chem.*, **29**, 295 (1899).

The reaction

$$H_2 + CO_2 = CO + H_2O$$

has been studied very extensively, as it is of technical importance both in the manufacture of "water gas" and in the manufacture of hydrogen from water gas. The most important data are those of Hahn [1] and of Haber and Richardt [2] whose investigations combined cover the temperature range of about 600° C. to 1500° C.

The experimental method of Hahn consisted in allowing a slow stream of gases, of known composition, to pass over a catalyst, and in then cooling the gases rapidly and analyzing them. Characteristic data taken for the temperature of 980° C. are given in Table II and illustrate very well the relation existing between the partial pressures of the reacting gases at equilibrium. In these particular experiments the initial gases were mixtures of CO_2 and H_2 in varying proportions, and therefore in the equilibrium mixture the CO and H_2O are of equal volume percentage. The values of K_p calculated from the equation

$$K_p = \frac{P_{CO} \times P_{H_2O}}{P_{CO_2} \times P_{H_2}} \tag{122}$$

show only irregular variations from the mean of 1.60.

The effect of temperature upon the equilibrium was investigated by both Haber and Hahn and their data have been recalculated by both Haber [3] and by Lewis and Randall.[4]

The latter authors have shown that the variation of the equilibrium constant with the temperature is well represented by an equation of the form of equation (79).

Their equation is

$$lnK_p = -\frac{10{,}100}{RT} + \frac{1.81 lnT}{R} - \frac{0.00445T}{R} + \frac{0.00000068T^2}{R} + 0.272. \tag{123}$$

Values of K_p calculated from equation (123) show a rapid change in the values of the equilibrium constant with the temperature, the equilibrium being displaced largely toward the right at high temperatures, and to the left at low temperatures. In the technical preparation of hydrogen by means of this reaction, the starting point is usually a mixture of CO and H_2 in approximately equivalent proportions. It is desired to obtain from it a mixture as low in CO and as high in H_2 as possible. From considerations of equations (122) and (123) it is clear that this result may be achieved by operating at as low a temperature as possible, and by adding steam (which may later be

[1] *Z. physik. Chem.*, **44**, 513 (1904); **48**, 735 (1904).

[2] *Z. anorg. Chem.*, **38**, 5 (1904).

[3] Haber, Thermodynamics of Technical Gas Reactions (tr.), Longmans, Green & Co., 1908.

[4] Lewis and Randall, Thermodynamics and Chemistry, McGraw Hill Co., 1923, p. 574.

removed readily) to the mixed gases. The limits to which these procedures may be effective commercially are determined by the rate of reaction at low temperatures, by the cost of steam, etc.[1]

TABLE II

EQUILIBRIUM DATA IN WATER GAS REACTION
Temperature = 986° C.

Initial Composition Per Cent by Volume		Equilibrium Composition Per Cent by Volume		
CO_2	H_2	CO_2	$CO = H_2O$	H_2
10.1	89.9	0.70	9.46	80.38
		0.67	9.33	80.67
30.1	69.9	7.18	23.00	46.82
		7.12	22.92	47.04
49.1	51.9	21.52	27.83	22.82
		20.78	28.04	23.14
		21.36	27.88	22.87
60.9	39.1	34.67	26.25	12.77
		34.20	26.61	12.58
70.3	29.7	47.66	22.79	6.76
		47.35	22.85	6.95

Another reaction of this class, which is of industrial importance, is that between nitrogen and oxygen, in accordance with the equation

$$\tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 = NO. \qquad (124)$$

The rate at which equilibrium is established for the reaction is extremely slow and it has been measured directly only at temperatures of 1500° C. and above.[2] Even at these temperatures the percentage of nitric oxide produced by heating air until equilibrium is established is extremely small, being 0.377 at 1540° C. and 2.33 at 2400° C. At any given temperature the per cent of nitric oxide in equilibrium could be increased somewhat by heating a 1 : 1 mixture of N_2 and O_2 (compare p. 454), but, in the technical utilization of the reaction for the fixation of nitrogen, the increased percentage of nitric oxide would not be sufficient to warrant the use of artificial $N_2 : O_2$ mixture instead of air. The variation of the equilibrium constant with the temperature is expressed by the equation

$$\ln K_p = -\frac{21{,}600}{RT} + \frac{2.50}{R}. \qquad (125)$$

[1] For a discussion of the technical problem the reader is referred to Taylor, Industrial Hydrogen, Chemical Catalog Co., 1921. Later data on the water-gas equilibrium are to be found in *J. Am. Chem. Soc.*, **46**, 888 (1924).

[2] Nernst, *Z. anorg. Chem.*, **49**, 213 (1906).

Since the heat capacities of nitrogen and oxygen are identical with that of nitric oxide, the heat of the reaction does not vary with the temperature, and the characteristic equation assumes the simple form given above.

Reactions in which the Total Number of Molecules Changes: A great number of gas reactions of this type have been the subject of experimental investigation. In illustration may be cited the following:

$$CO + \tfrac{1}{2}O_2 = CO_2, \qquad (126)\ [1]$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O, \qquad (127)\ [2]$$
$$N_2O_4 = 2NO_2, \qquad (128)\ [3]$$
$$NO_2 = NO + \tfrac{1}{2}O_2, \qquad (129)\ [4]$$
$$I_2 = 2I, \qquad (130)\ [5]$$
$$(CH_3COOH)_2 = 2CH_3COOH, \qquad (131)\ [6]$$
$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 = NH_3, \qquad (132)\ [7]$$
$$SO_2 + \tfrac{1}{2}O_2 = SO_3, \qquad (133)\ [8]$$
$$HCl + \tfrac{1}{4}O_2 = \tfrac{1}{2}Cl_2 + \tfrac{1}{2}H_2O. \qquad (134)\ [9]$$

Certain of these reactions will be discussed in some detail to illustrate experimental method and to point out the applications of the equilibrium laws to practical problems.

When the equation is so written as to indicate the breaking up of a single molecular species into either more than one molecule of an individual substance (equations (128), (130) and (131)) or into more than one kind of molecule (equations (129) and (126), (127), (132) and (133) written in the opposite sense), the reaction is frequently termed a *dissociation*, and the equilibrium constant is called the dissociation constant. In examining values for equilibrium constants occurring in the literature, care should always be taken to

(These references are not complete; they refer to the more important investigations.)

[1] Nernst and von Wartenburg, *Z. physik. Chem.*, **56**, 548 (1906).
Langmuir, *J. Am. Chem. Soc.*, **28**, 1357 (1906).
Lowenstein, *Z. physik. Chem.*, **54**, 797 (1905).

[2] Nernst and von Wartenburg, *Nacht. Kgl. ges. Wiss.*, Gottingen (1905).
Lowenstein, *Z. physik. Chem.*, **56**, 513 (1906).
Langmuir, *J. Am. Chem. Soc.*, **28**, 1357 (1906).

[3] Schreber, *Z. physik. Chem.*, **24**, 651 (1897).
Bodenstein and Katayama, *Z. Elektrochem.*, **15**, 244 (1909).
Bodenstein, *Z. anorg. Chem.*, **100**, 68 (1922).

[4] Bodenstein and Katayama (*loc. cit.*); Bodenstein (*loc. cit.*).

[5] Stark and Bodenstein, *Z. Elektrochem.*, **16**, 961 (1910).

[6] Drucker and Ullmann, *Z. physik. Chem.*, **74**, 567 (1910).

[7] Haber, *Z. Elektrochem.*, **20**, 592 (1914).
Haber, Tamaru and Ponnay, *Z. Elektrochem.*, **21**, 89 (1915).
Haber and Maschke, *Z. Elektrochem.*, **21**, 129 (1915).
Haber and Greenwood, *Z. Elektrochem.*, **21**, 241 (1915).
Larson and Dodge, *J. Am. Chem. Soc.*, **45**, 2918 (1923).
Larson, *J. Am. Chem. Soc.*, **46**, 367 (1924).

[8] Bodenstein and Pohl, *Z. Elektrochem.*, **11**, 373 (1905).

[9] Lunge and Marmier, *Z. angew. Chem.*, **10**, 105 (1897).
Lewis, *J. Am. Chem. Soc.*, **28**, 1380 (1906).
von Falkenstein, *Z. physik. Chem.*, **59**, 313 (1907).

note the direction in which the reaction is written, and also the exact equilibrium constant employed, for the numerical values of K_p, K_c and K_x are not identical for reactions in which the number of molecules changes, as previously shown.

Dissociation of Carbon Dioxide: The reaction

$$CO + \tfrac{1}{2}O_2 = CO_2 \tag{135}$$

goes ordinarily so nearly to completion from left to right that direct measurement of the equilibrium constant represents a difficult experimental problem. Nevertheless, very satisfactory data have been obtained by Nernst and his students. Nernst and von Wartenburg passed carbon dioxide through a heated tube and then, after rapid cooling, analyzed the gases formed; Langmuir passed carbon dioxide either alone or mixed with carbon monoxide or oxygen, around a heated platinum wire at high velocity, and analyzed the issuing gases; Lowenstein made use of the Victor Meyer apparatus. Their measurements cover the range of 1100° C. to 1450° C. Pure carbon dioxide is dissociated at atmospheric pressure to the extent of only 0.4 per cent at the highest temperature measured, and is only 0.0142 per cent dissociated at 1100° C.

These data are in very good agreement with calculations of the equilibrium made indirectly by combination of other data.

The equation[1]

$$lnK_p = \frac{67{,}510}{RT} - \frac{2.75lnT}{R} + \frac{0.0028T}{R} + \frac{0.00000031T^2}{R} - \frac{4.46}{R} \tag{136}$$

expresses quite accurately the variation of the equilibrium constant with the temperature.

The dissociation of carbon dioxide will vary with the total pressure, as shown in an earlier section. If a represents the fraction of carbon dioxide dissociated, then we may write the mass law equation

$$K_p = \frac{P_{CO_2}}{P_{CO} \times P_{O_2}^{1/2}} = \frac{(1-a)P}{aP(0.5aP)^{1/2}} = \frac{\sqrt{2}(1-a)}{a^{3/2} \times P^{1/2}}. \tag{137}$$

For values for which a is small as compared with unity, we may write this equation

$$a = \frac{K}{P^{1/3}}. \tag{138}$$

The dissociation varies, then, inversely with the 1/3 power of the total pressure.

Dissociation of Water Vapor: The reaction

$$H_2 + \tfrac{1}{2}O_2 = H_2O \tag{139}$$

[1] Lewis and Randall, Thermodynamics and Chemistry, McGraw Hill Co. (1923).

proceeds even more nearly to completion than reaction (135), but its equilibrium has been measured by the same methods and the same investigators as those cited in the preceding case. In addition, Lowenstein, making use of the fact that hydrogen gas passes readily through hot platinum, measured directly the partial pressure of hydrogen in equilibrium with water vapor and oxygen. The data show that water vapor is dissociated at atmospheric pressure to less than 0.01 per cent at 1100° C. and the dissociation has risen to only 1.8 per cent at 2000° C.

This important reaction has been the subject of many indirect measurements and the data from all sources agree admirably with the equation

$$lnK_p = \frac{57{,}410}{RT} - \frac{0.94 lnT}{R} - \frac{0.00165T}{R} + \frac{0.00000037T^2}{R} - \frac{3.92}{R}. \quad (140)$$

The Dissociation of Nitrogen Tetroxide: Nitrogen tetroxide is appreciably dissociated at 0° C.,

$$N_2O_4 = 2NO_2, \quad (141)$$

and the amount of dissociation increases rapidly with increasing temperature. The experimental measurement of the equilibrium conditions has thus been very simple, and, as a result, the literature contains many references to the reaction. The measurements have usually involved the determination of the density of the gas, and, as the method is one of the most frequently used in studying equilibria in gas reactions in which the total number of molecules changes, it may be considered in some detail.

The density (gm./liter) of any gas which obeys the gas laws is given by the equation

$$d_t = \frac{MP}{RT}, \quad (142)$$

where M is the molecular weight and P the total pressure. This density we may call the theoretical density, d_t. If dissociation occurs, the volume will increase in proportion to the increase in the total number of molecules, and since the total weight remains constant, the density will decrease in the same proportion. In the case of one mol. N_2O_4, if a is the fraction dissociated, $1 - a$ will be the number of mols. of undissociated gas, and $2a$ will be the number of mols. of NO_2. The total number of mols. will be $1 + a$, and the observed density will bear the relation to the theoretical density

$$\frac{d_0}{d_t} = \frac{1}{1 + a}. \quad (143)$$

Rearranging, we have

$$a = \frac{d_t - d_0}{d_0}. \quad (144)$$

The dissociation constant K_p is given by the equation

$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{\left(\frac{2a}{1+a}P\right)^2}{\left(\frac{1-a}{1+a}\right)P} = \frac{4a^2P}{(1-a^2)}. \quad (145)$$

In this case the dissociation (a) varies, when the dissociation is small, inversely as the square root of the pressure.

It should be noted that if a substance dissociates into N molecules instead of 2 as in the case above, equation (144) becomes

$$a = \frac{d_t - d_0}{(N-1)d_0}. \quad (146)$$

The values of K_p for the dissociation are 0.0154 at 0° C. and 13.33 at 100° C.; the variation with the temperature for this range is given by the equation

$$lnK_p = -\frac{13{,}600}{RT} + \frac{41.6}{R}. \quad (147)$$

The Dissociation of Nitrogen Dioxide: At temperatures of 150° C. and more, nitrogen dioxide begins to be measurably dissociated into nitric oxide and oxygen, the reaction occurring according to equation (148),

$$NO_2 = NO + \tfrac{1}{2}O_2. \quad (148)$$

The value of the equilibrium constant is of some technical importance, as the reverse reaction occurs at one stage in the preparation of nitric acid from nitric oxide, formed either by oxidation of atmospheric nitrogen (see p. 448) or by oxidation of ammonia. The equilibrium constant has been measured by Bodenstein and Katayama (*loc. cit.*), and later by Bodenstein (*loc. cit.*), from careful determinations of the density of the reaction mixture. The temperature range in the latter work was 220° C. to 550° C. Above 550° C., the measurements were made uncertain by partial decomposition of the nitric oxide into nitrogen and oxygen. The data of Bodenstein are well represented by the empirical equation

$$lnK_p = -\frac{5749}{T} + 1.75\,lnT - 0.00050T + 2.839. \quad (149)$$

The equation employed by Lewis and Randall is

$$lnK_p = -\frac{14{,}170}{RT} + \frac{2.75lnT}{R} - \frac{0.0028T}{R} + \frac{0.00000031T^2}{R} + \frac{2.73}{R}. \quad (150)$$

The Ammonia Equilibrium: This reaction has received a large amount of attention because of its great importance for the commercial synthesis of ammonia,

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 = NH_3. \tag{151}$$

The success which has attended this industry is a striking example of the value of the application of principles of physical chemistry to a technical problem. At first sight, the reaction would appear to be impossible as a source of commercial ammonia, for nitrogen and hydrogen do not combine at measurable rates at low temperatures. At temperatures at which the rate of reaction is appreciable, the percentage of ammonia at equilibrium at atmospheric pressure is inappreciable.

If we write the equation

$$K_p = \frac{P_{NH_3}}{P_{H_2}^{3/2} \times P_{N_2}^{1/2}}, \tag{152}$$

it is clear that the partial pressure of the ammonia at equilibrium will be increased by increasing the total pressure. This is brought out by considering the special case in which hydrogen and nitrogen are present in the ratio of 1 : 3 (which gives the maximum per cent of NH_3 possible at any given temperature and pressure, as shown in a preceding section. If the volume fraction of ammonia present in the gas at equilibrium is denoted by a, and if P is the total pressure, we may write equation (152) [1]

$$\frac{a}{(1-a)^2} = KP. \tag{153}$$

When a is small compared with unity, it varies almost directly with the total pressure. By operating at pressures of 30 atmospheres, Haber and his students (*loc. cit.*) were able to determine values of the equilibrium constant with considerable accuracy. Recent investigations by Larson, and Larson and Dodge (*loc. cit.*), have included measurements of the equilibrium constant up to 1000 atmospheres pressure, under conditions in which the gas laws no longer hold. These data are discussed further below.

The variation of the equilibrium constant with the temperature may be expressed with fair accuracy by a simple equation, suggested by Haber, namely,

$$ln K_p = \frac{13{,}200}{RT} - 6.134. \tag{154}$$

From the data of Haber, and from consideration of the heat capacities of the reacting gases, Lewis and Randall (*loc. cit.*) propose the equation

$$ln K_p = \frac{9500}{RT} - \frac{4.96 ln T}{R} - \frac{0.000575T}{R} + \frac{0.00000085T^2}{R} + \frac{9.61}{R}. \tag{155}$$

[1] Tour, *J. Ind. Eng. Chem.*, **13**, 298 (1921).

Larson and Dodge have also proposed empirical equations representing their own data at different pressures. Obviously, low temperatures and high pressure increase rapidly the proportion of ammonia at equilibrium, and the success of the industry of ammonia synthesis has been achieved by the development of catalysts which permit moderate temperatures of operation, and of apparatus for carrying out the reaction between 100 and 1000 atmospheres pressure.

The Oxidation of Sulphur Dioxide: The equilibrium in this reaction

$$SO_2 + \tfrac{1}{2}O_2 = SO_3 \tag{156}$$

has been the subject of many careful investigations, particularly because of its bearing upon the "contact" process for the manufacture of sulfuric acid. The experimental method has usually consisted in passing a mixture of sulfur dioxide and oxygen, alone or mixed with nitrogen, over a catalyst of finely divided platinum, and then analyzing the gases after rapid cooling. The earlier investigations of Knietsch [1] have been superseded by the more accurate work of Bodenstein and Pohl (*loc. cit.*), who carried out very careful determinations of the equilibrium with various mixtures of sulphur dioxide, oxygen and nitrogen, over a range of temperature of about 500° C. to 800° C. Their data show that the equilibrium constant corresponds to that required by the equation

$$K_p = \frac{P_{SO_3}}{P_{SO_2} \times P_{O_2}^{1/2}}, \tag{157}$$

where the variation of K_p with the temperature is expressed by the equation (Lewis and Randall, *loc. cit.*)

$$lnK_p = \frac{22{,}600}{RT} - \frac{21.36}{R}. \tag{158}$$

In technical practice, it is desired to bring about as completely as possible the oxidation of the sulphur dioxide, possible variables being the composition of the mixture, the temperature and the pressure. It is instructive to write equation (157) as follows:

$$\frac{N_{SO_3}}{N_{SO_2}} = K_p \sqrt{\frac{N_{O_2}}{N} \times P}, \tag{159}$$

where N refers to the total number of mols. of gas present, the subscript identifying the individual gases. The term on the left of the equation (159) should have for commercial operation a value of the order of 50–100, which represents 98 to 99 per cent efficiency of oxidation. Obviously, the ratio of SO_3/SO_2 will increase with increase in total pressure, but only proportional to the square root of the total pressure, so that a great gain in efficiency is not to be expected from pressure change. The effect of the excess oxygen N_{O_2}, is also clear from

[1] Knietsch, *Ber.*, **34**, 4069 (1901); *Ber. V. Int. Kon. Angew. Chem.*, **1**, 617 (1904).

equation (159). If N_{O_2} should be extremely small, it might reduce the efficiency of oxidation considerably, but unless this is the case, changes in N_{O_2}, do not alter appreciably the SO_3/SO_2 ratio; for, an increase in N_{O_2} also increases N, and the SO_3/SO_2 ratio is proportional only to the square root of this ratio. If N_{O_2} is increased by adding *air* (essentially one O_2 to four N_2), the ratio of N_{O_2}/N may be *decreased* instead of increased, and the efficiency of oxidation affected unfavorably. Obviously, therefore, with a moderate excess of oxygen and at moderate pressures, the only way in which a high equilibrium value of the SO_3/SO_2 ratio may be obtained is by operating under temperature conditions for which K_p has a high value. Technically, the reaction is carried out so that the temperature of the gas issuing from the reaction system is about 425° C. to 450° C., where K_p has values of about 237 and 135 respectively.

The Oxidation of Hydrogen Chloride: The oxidation of hydrochloric acid gas by oxygen which occurs readily at temperatures around 400° C. in the presence of cupric chloride as a catalyst has become an industry of importance for the commercial preparation of chlorine, by the Deacon process.

$$HCl + \tfrac{1}{4}O_2 = \tfrac{1}{2}Cl_2 + \tfrac{1}{2}H_2O. \tag{160}$$

Investigations by Lewis (*loc. cit.*), von Falkenstein (*loc. cit.*), and others have shown that the condition of equilibrium corresponds to that required by the equation

$$K_p = \frac{P_{Cl_2}^{1/2} \times P_{H_2O}^{1/2}}{P_{HCl} \times P_{O_2}^{1/4}}. \tag{161}$$

In practice, mixtures of hydrochloric acid gas and air are passed over the catalyst, and the undecomposed hydrogen chloride is absorbed by water. In considering the extent to which the hydrochloric acid may be oxidized, it is somewhat convenient to transform equation (161).

If we multiply numerator and denominator by $P_{Cl_2}^{1/2}$, and rearrange, we obtain

$$\frac{P_{Cl_2}}{P_{HCl}} \times \frac{1}{P_{O_2}^{1/4}} \times \frac{P_{H_2O}^{1/2}}{P_{Cl_2}^{1/2}} = K_p. \tag{162}$$

If we consider 1 mol. of HCl, and if x represents the fraction decomposed, the ratio P_{Cl_2}/P_{HCl} becomes $x/2(1 - x)$. If the initial gas mixture is dry, $P_{Cl_2} = P_{H_2O}$, and equation (162) may be written

$$\frac{x}{(1-x)} = 2K_p\left(\frac{N_{O_2}}{N}\right)^{1/4} \times P^{1/4}. \tag{163}$$

The effect upon the efficiency of oxidation of changes in the pressure, and addition of oxygen or air, is clearly shown by this equation.

The variation of K_p with the temperature is calculated by Lewis and Randall to follow the equation

$$lnK_p = \frac{6835}{RT} - \frac{0.02lnT}{R} - \frac{0.00085T^2}{R} + \frac{0.000000185T^2}{R} - \frac{7.27}{R}. \tag{164}$$

Gaseous Reactions at High Pressures: The equation for the law of mass action (Equation 4) expressing the dynamic nature of equilibrium

$$\frac{K_1}{K_2} = K = \frac{A_C \times A_D}{A_A \times A_B}$$

may obviously be expected to be valid under conditions in which the gas laws are approximately obeyed. If the partial pressure of a gas differs markedly from the activity, it is not to be expected that the "constant" of equation (4) will be strictly independent of the initial proportions of the reacting substances, or of the total pressure. Most equilibria in gaseous systems have been measured at fairly high temperatures and low pressures, where the gas laws are approximately valid for nearly all gases, but at least one equilibrium, that of the technically important reaction

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 = NH_3, \qquad (164)$$

has been measured at quite high pressures, the recent measurements of Larson and of Larson and Dodge [1] extending the range of experimental data to 1000 atmospheres pressure. It is interesting to consider their data, some of which are given in Table III and Table IV.

TABLE III

PER CENT OF NH_3 IN EQUILIBRIUM WITH A 1 : 3, N_2–H_2 MIXTURE

Temperature ° C.	Pressures in Atmospheres						
	10	30	50	100	300	600	1000
325	10.38						
350	7.35	17.80	25.11				
375	5.25	13.35	19.44	30.95			
400	3.85	10.09	15.11	24.91			
425	2.80	7.59	11.71	20.23			
450	2.04	5.80	9.17	16.36	35.5	53.6	69.4
475	1.61	4.53	7.13	12.98	31.0	47.5	63.5
500	1.20	3.48	5.58	10.40	26.2	42.1	—

The extent of deviation of the reacting gases and mixtures of the same over the range of pressures 0–1000 atm. and temperatures up to 400° C. has been the objective of a considerable amount of recent research.[2] At 1000 atmospheres the PV/P_0V_0 ratio reaches 2.0641 in the case of nitrogen, 1.7107 for hydrogen and 1.8029 for a 3 : 1, H_2-N_2 mixture at 0° C. At 300° C. and 1 atm., PV/P_0V_0 is in all cases 2.0978 and this value rises to 3.3195 for nitrogen,

[1] *J. Am. Chem. Soc.*, **45** 2918 (1923); **46**, 367 (1924).

[2] Verschoyle, *Proc. Roy. Soc.*, **111A**, 552 (1926); Bartlett, *J. Am. Chem. Soc.*, **49**, 65, 687, 1955 (1927); **50**, 1275 (1928).

TABLE IV

EQUILIBRIUM CONSTANT

$$K_p = \frac{P_{NH_3}}{P_{N_2}^{1/2} \times P_{H_2}^{3/2}}$$

Temperature ° C.	Pressures in Atmospheres						
	10	30	50	100	300	600	1000
350	0.0266	0.0273	0.0278				
375	0.0181	0.0184	0.0186	0.0202			
400	0.0129	0.0129	0.0130	0.0137			
425	0.00919	0.00919	0.00932	0.00987			
450	0.00659	0.00676	0.00690	0.00725	0.00884	0.01294	0.02328
475	0.00516	0.00515	0.00513	0.00532	0.00674	0.00895	0.01493
500	0.00381	0.00386	0.00388	0.00402	0.00498	0.00651	

2.8125 for hydrogen and 2.9495 for the 3 : 1 mixture when the pressure is raised to 1000 atm. at 300° C. With ammonia, the deviations may be expected to be much larger. It is obvious that with increasing pressure and decreasing temperature not only are the deviations of all gases greater but also the proportion of ammonia in the equilibrium mixture will increase. It is therefore to be expected that the value for K_p will show a greater variation with the pressure at the lower temperature than at the higher temperatures. This is borne out by the data in Table IV, from which it appears that K_p at 375° C. increases by about 10 per cent in changing from 10 atmospheres to 100 atmospheres, while at 500° C. the variation is about one-half that value. The value at 450° C. at 600 atmospheres is nearly twice that at 10 atmospheres, while at 500° C. the value at 600 atmospheres is about 1.7 times that at 10 atmospheres. The fact that the constant increases with increasing pressure indicates that the ratio of the partial pressure of ammonia to its activity, P_{NH_3}/a_{NH_3}, increases more rapidly with the pressure than the corresponding ratios for nitrogen and hydrogen, as would be expected from the known equation of state of ammonia at lower temperatures. The activity constant, K_a, which must be independent of the pressure, is presumably more nearly given by the values of K_p at the lower pressures.

It would be expected that at the very high pressures the values of K_p would also vary somewhat with the proportions of nitrogen, hydrogen and ammonia in the equilibrium mixtures, but, since all of the experiments were carried out on a mixture of nitrogen and hydrogen in the ratio of 1 : 3, the data do not permit this point to be decided.

Similar studies of equilibrium at high pressures in the system hydrogen-carbon monoxide-methanol have been prompted by the recent industrial developments in this field. The most recent determinations of Newitt, Byrne and Strong [1] yielded data on the equilibrium by a static and by an intermittent

[1] *Proc. Roy. Soc.*, **123A**, 236 (1929).

flow method at pressures in the neighborhood of 100 atmospheres, equilibrium being approached from both the methanol and the mixed gas sides. A range of temperatures from 280 to 388° C. was covered. The final data, when plotted for $ln\ K_p$ against the reciprocal of the absolute temperature, gave a straight line, indicating that, over the temperature range in question, the free energy might be represented by an equation linear with respect to temperature of the form

$$\Delta F = 70.5T - 30500.$$

This equation gives the following data for K_p at the various temperatures.

Temp° C.	260	280	300	320	340	360	380
K_p	1.2×10^{-3}	4.5×10^{-4}	1.6×10^{-4}	6.7×10^{-4}	2.9×10^{-5}	1.3×10^{-5}	6.3×10^{-6}

These results differ materially from those of earlier workers and calculations made by others.[1] Smith and Branting give as the free energy equation

$$\Delta F = -20857 + 41.17 \log T - 0.01423\ T^2 - 54.42\ T.$$

Their data give $K_p = 6.51 \times 10^{-4}$ at 300° C.; Audibert and Raineau give $K_p = 11.3 \times 10^{-4}$; Christiansen's data give 4.27×10^{-4} compared with 1.6×10^{-4} of the preceding table. The calculations of Kelley are far from the experimental results giving 8.2×10^{-2}.

All these data were deduced without taking into account the deviations from the gas laws. Isotherms for hydrogen, carbon monoxide and mixtures of the two have now been obtained by Scott,[2] so that, with the compressibility data of Ramsay and Young [3] for methanol, it is now possible to estimate actual practical yields with a further degree of accuracy than before. Without these refinements Newitt, Byrne and Strong calculated an equilibrium mixture of 36.4 atm. CH_3OH, 54.6 atom. CO and 109 atm. H_2 for the equilibrium at 200 atm. total pressure and 600° K. Smith and Branting's data, which are higher than these, indicate an increase in yield due to compressibility of the gases from 71 per cent uncorrected to 80 per cent corrected conversion of CO to CH_3OH. This example parallels the case of ammonia synthesis just considered in that the product is the most compressible gas of the three and hence, with increasingly high pressures, the value of K_p will be expected to rise rapidly.

Homogeneous Equilibrium in the Liquid Phase

One of the first experimental investigations of equilibrium was that of Berthelot and Pèan de St. Gilles (*loc. cit.*) who carried out an extensive study of the reaction between acetic acid and ethyl alcohol, proved it to be reversible,

[1] Kelley, *Ind. Eng. Chem.*, **18**, 78 (1926); Christiansen, *J. Chem. Soc.*, **128**, 413 (1926); Morgan, Taylor and Hedley, *J. Soc. Chem. Ind.*, **47**, 117 T (1928); Audibert and Raineau, *Ann. Office Combustibles Liquides*, 1927, Part 4; Lewis and Frohlich, *Ind. Eng. Chem.*, **20**, 285 (1928); Smith and Branting, *J. Am. Chem. Soc.*, **51**, 129 (1929).

[2] *Proc. Roy. Soc.*, **125A**, 330 (1929).

[3] Int. Crit. Tables, Vol. III, p. 436.

and showed that their equilibrium data could be represented mathematically by the equation

$$K = \frac{\text{mols. ester} \times \text{mols. water}}{\text{mols. acid} \times \text{mols. alcohol}}, \tag{165}$$

which we recognize as identical with equation (38), remembering that the number of mols. of reactants and resultants are equal. Berthelot and Pèan de St. Gilles mixed alcohol and acetic acid in varying proportions in sealed glass tubes, and heated the tubes at temperatures in the neighborhood of 200° C. until no further change in composition was brought about by further heating. They then analyzed the mixtures for acetic acid, and calculated the composition of the entire mixture from this measurement. If a represents the number of mols. of alcohol taken, b the number of mols. of acetic acid, and x the number of mols. of ester (or water) formed, their experiments show that at equilibrium the proportions of all constituents present are quite closely given by the equation

$$K = \frac{x^2}{(a - x)(b - x)}, \tag{166}$$

where K has the numerical value of 4.0. Table I gives the results of a series of experiments, showing the values of x determined experimentally, and those calculated from equation (166). The agreement is probably within the experimental error, and shows that for the system in question under the conditions of measurement, the activity of the reacting species is approximately proportional to the mol. fraction.

TABLE V[1]

Mols. Acetic Acid Taken a	Mols. Alcohol Taken b	Mols. Ester Formed x (Found)	Mols. Ester Calculated x
1.0	0.05	0.05	0.049
1.0	0.18	0.171	0.171
1.0	0.33	0.293	0.301
1.0	0.50	0.414	0.423
1.0	1.00	0.667[2]	0.667
1.0	2.00	0.858	0.850
1.0	8.00	0.966	0.970

Berthelot and Pèan de St. Gilles found the value of the equilibrium constant to be practically independent of the temperature, a fact confirmed by later investigators,[3] and in accord with the known fact that the heat of reaction must

[1] Recalculated by van't Hoff, *Ber.*, 10, 669 (1877).
[2] Used in obtaining the value for K.
[3] Miss Tobin, Dissertation, Bryn Mawr College (1917).

be very close to zero, as shown indirectly by consideration of the heats of combustion of alcohol, acetic acid, and ethyl acetate.

The equilibrium constants for esterification reactions have been measured perhaps more frequently than is the case for any other type of reaction in liquid systems (excluding ionic equilibria), and the literature contains values for the equilibrium constants for the reactions between nearly all of the common acids and alcohols.[1] One or two cases are of special interest in illustrating the application of the mass law.

It has been shown by Menschutkin that esters of tertiary alcohols decompose usually into acid and unsaturated hydrocarbon, and the equilibrium conditions for such reactions have been studied by Konowalow,[2] and by Nernst and Hohmann.[3] The latter authors measured the equilibrium of the reaction between amylene and the chlorinated acetic acids, their results on trichloracetic acid at 100° C. being characteristic. The reaction proceeds according to the equation

$$CCl_3COOH + C_5H_{10} = CCl_3.COOC_5H_{11}, \tag{167}$$

and we may write for it the mass law expression:

$$K_X = \frac{X \text{ ester}}{X \text{ acid} \times X \text{ amylene}}. \tag{168}$$

If 1.0 mol. of acid is mixed with a mols. of amylene, and if x represents the mols. of ester formed when the reaction has reached equilibrium, we may write equation (168) as

$$K_x = \frac{x \times N}{(a - x)(1 - x)}, \tag{169}$$

where N represents the total number of mols. Table VI contains a comparison

TABLE VI

Equilibrium Data

($CCl_3COOH + C_5H_{10} = CCl_3COOC_5H_{11}$)

Mols. C_5H_{10} a	Mols. CCl_3COOH	Mols. Ester x (Found)	Mols. Ester x (Calculated)
2.15	1.0	0.762	0.762
4.12	1.0	0.814	0.821
4.48	1.0	0.820	0.826
6.63	1.0	0.838	0.844
6.80	1.0	0.839	0.845
7.13	1.0	0.855	0.846

[1] Menschutkin, *Ann. Chim. Phys.*, [5] **20**, 227 (1880); **23**, 14 (1881); **30**, 81 (1883).
[2] *Z. physik. Chem.*, **1**, 63 (1887); **2**, 6, 380 (1888).
[3] *Z. physik. Chem.*, **11**, 352 (1893).

of the values for x found experimentally for several values of a, and also those calculated from the mean value of the equilibrium constant.

It is clear that there is very fair agreement between the observed and calculated values.

A comparison of these data with those on p. 459 for the reaction between acetic acid and ethyl alcohol brings out an interesting difference in behavior. In the latter case the mols. of ester present at equilibrium increase rapidly with increasing mols. of alcohol added, and approach unity as the number of mols. of alcohol becomes large. In the case of the reaction between amylene and acid, the number of mols. of ester changes very slowly with an increase in the number of mols. of amylene. The reason is clear from comparison of equations (166) and (169). In equation (169) an increase in a produces an increase in N, and therefore x is much less affected than in the case of equation (166). In fact it can be shown that a might be made to approach infinity without increasing the value of x to more than about 0.88, provided equation (169) is valid over the entire range of concentrations.

The Effect of the Solvent: Many reactions in liquid media are carried out in the presence of a large excess of some indifferent constituent called the solvent. The theoretical implications of the addition of indifferent substances to equilibria have already been discussed, but the case of the solvent deserves particular consideration, as many experimental data are available upon equilibria in reactions in different media.

If we consider equations (106) and (107) and neglect the total pressure, we have

$$K_x = \frac{N_C{}^c \times N_D{}^d \cdots}{N_A{}^a \times N_B{}^b \cdots} \times N^{(a+b-c-d)} \tag{170}$$

and

$$K_c = \frac{N_C{}^c \times N_D{}^d}{N_A{}^a \times N_B{}^b} \times V^{(a+b-c-d)}. \tag{171}$$

From these equations it is clear that so long as the activity is equal to or proportional to the mol. fraction or the molecular concentration, addition of a solvent (which affects N and V) will be entirely without effect upon any equilibrium in which $a + b = c + d$. Berthelot and Pèan de St. Gilles found this to be the case for the reaction between acetic acid and alcohol, using acetone as a solvent. If $a + b$ is not equal to $c + d$, the equilibrium concentrations will vary with the amount of solvent in accordance with equations (170) and (171), the equilibrium constants being unaffected. However, it frequently happens that the solvent may exercise a very marked influence upon the activity of some one or more of the reacting species, so that the relation between the mol. fraction and the activity no longer exists, and equations (170) and (171) are not valid. If the influence is sufficiently definite, we may, however, substitute another equilibrium equation. Thus, some reacting species may exist in a different molecular state in different solvents. Let us consider the general reaction

$$aA + bB = cC + dD, \tag{172}$$

for which in the absence of a solvent or in the presence of a really indifferent solvent we may write

$$K_x = \frac{X_C{}^c \times X_D{}^d}{X_A{}^a \times X_B{}^b}. \tag{173}$$

Let us consider this reaction carried out in a solvent in which the substance A exists almost entirely in the form of double molecules. For the equilibrium between single and double molecules we have the relation

$$K = \frac{X_A{}^2}{X_{(A_2)}}. \tag{174}$$

Now if X_A is very small as compared with $X_{(A_2)}$, that is, if nearly all of A is in the form of (A_2), we may write

$$X_A = K'\left(\frac{0.5N_A}{N}\right)^{1/2}, \tag{175}$$

where N_A represents the total number of mols. of A, calculated without regard to the molecular condition of A. If we substitute the value of X_A in equation (173), we obtain

$$K_x' = \frac{X_C{}^c \times X_D{}^d \cdots}{X_{(A_2)}{}^{a/2} \times X_B{}^b \cdots}, \tag{176}$$

where $X_{(A_2)}$ has the value of $\frac{0.5N_A}{N}$. We might have obtained this same equation by neglecting the single molecules of A entirely, and writing the reaction

$$\tfrac{1}{2}a(A_2) + bB \cdots = cC + dD \cdots, \tag{177}$$

for which the mass law equation would be

$$K_x = \frac{X_C{}^c \times X_D{}^d \cdots}{X_{(A_2)}{}^{a/2} \times X_B{}^b}. \tag{178}$$

Equations (176) and (178) are evidently identical.

An example of a case of this type is given by the experiments of Nernst and Hohmann (*loc. cit.*) upon the esterification of amylene dissolved in benzene. The normal reaction of amylene and trichloracetic acid in the absence of a solvent proceeds according to equation (167), and the equilibrium relations are expressed by equations (168) and (169). In benzene solution, the acid exists almost entirely as double molecules, while the other substances behave normally.

If we mix together a mols. of amylene with 1.0 mol. of trichloracetic acid, and bring the mixture to equilibrium in benzene solution, we find the equilibrium no longer expressed by equation (169), but by the equation

$$K_x' = \frac{xN^{1/2}}{(a - x)(1 - x)^{1/2}}, \tag{179}$$

where K_x' has evidently a different numerical value from that of K_x in equation (169).

The actual equilibrium condition for a given reaction may obviously vary greatly with the nature of the solvent in which the reaction takes place, particularly if a marked difference exists in the molecular condition of the reacting species in the two solvents.

A very similar relation holds for reactions which may occur in the gaseous phase as well as in the liquid phase. Thus it has been shown that the equilibrium constant for the reaction between acetic acid and alcohol is very different in numerical value for the gaseous reaction from the value obtained for the reaction in the liquid phase.[1]

Mathematical Treatment of Equilibrium Data

When the equilibrium constant for a reaction has been determined, the calculation of the extent to which the reaction may proceed at that temperature, for different mixtures of the reacting constituents, is, in general, obvious. Examples have been touched upon in the preceding sections. The use of equations (70) and (79) and of the empirical equations representing the equilibrium constant as a function of temperature also necessitates no particular emphasis. The *indirect* calculation of equilibrium conditions, from consideration of the free energy decrease involved in the formation of chemical compounds, has such important possibilities that some further discussion seems justified.

The free energy increase accompanying a chemical reaction is ordinarily measurable by one of three methods, as indicated previously in an earlier section. It is related to the equilibrium constant by the equation

$$\Delta F = -RTlnK_a. \tag{180}$$

It is related to the electromotive force of a reversible cell, in which the chemical reaction in question occurs through the operation of the cell, by the equation

$$\Delta F = -\mathbf{NFE} \tag{181}$$

(**N** is the number of faradays (**F**), equivalent to the reaction; **E**, the electromotive force).

It is related to the heat of reaction and the entropy change by the equation

$$\Delta F - \Delta H = -T\Delta S, \tag{182}$$

where ΔS is the increase in entropy.

Now the increase in free energy is a quantity determined by the initial and final states of the system, and therefore, when we write an equation expressing some definite change of state, the free energy increase accompanying the change is thereby fixed, whether or not it may be experimentally possible to carry out the reaction in question experimentally. Just as in thermo-

[1] Edgar and Schuyler, *J. Am. Chem. Soc.*, **46**, 64 (1924).

chemistry we can combine equations for the calculation of the heat of reactions, so we may combine equations for the calculation of free energy increase, and, from it, equilibrium data. For a complete study of this subject, reference should be made to Lewis and Randall's Thermodynamics and Chemistry, which contains a systematic tabulation of free energy data, but certain examples will be given from their calculations to illustrate the method employed. It is, of course, immaterial whether the reactions in question are homogeneous or heterogeneous.

The reaction

$$H_2 + \tfrac{1}{2}O_2 = H_2O$$

must be written to correspond to some definite change of state in order to fix the free energy increase. Since the temperature of 25° C. is one at which many experimental data are available, and since atmospheric pressure is the usual experimental condition, we may write the reaction

$$H_2\ (1\ \text{atm.}) + \tfrac{1}{2}O_2\ (1\ \text{atm.}) = H_2O\ (\text{gas},\ 1\ \text{atm.}). \qquad (183)$$

Let us consider the calculation of the free energy increase of the reaction at 25° C.

(*a*) Direct determinations of the equilibrium constant for the reaction have been made at high temperatures, as pointed out in a previous section. From the mean results of these data, and from the heat of reaction and the heat capacities of the reacting constituents, it is possible to calculate, through equation (80), the free energy change at 25° C., although the extrapolation is over a very wide temperature range, which will magnify the error in any of the quantities involved. The result of such a calculation gives

$$\Delta F_{25°\,C.} = -54{,}590\ \text{cal.}$$

(*b*) We may write the following series of equations, which added together give reaction (183):

$$\begin{aligned}
&(1) && 2Ag + \tfrac{1}{2}O_2 = Ag_2O,\\
&(2) && Ag_2O + H_2O_{(l)} = 2Ag^+ + 2OH^-,\\
&(3) && 2Ag^+ + 2(e) = 2Ag,\\
&(4) && H_2 = 2H^+ + 2(e),\\
&(5) && 2H^+ + 2OH^- = 2H_2O_{(l)},\\
&(6) && H_2O_{(l)} = H_2O_{(\text{gas})},
\end{aligned}$$

The free energy change for the first reaction has been determined by direct measurement of the equilibrium, over the temperature range of 300° C. to 500° C. From the equilibrium constant it is possible to determine the free energy increase, and through equation (80), the value at 25° C. may be calculated. The value thus obtained is $\Delta F = -2395$ cal.

The free energy increase at 25° C. of reaction 2 is calculable directly through the equilibrium constant, for the solubility of Ag_2O has been measured at this temperature. The value thus obtained is $\Delta F = 21{,}040$ cal.

The sum of the free energy increases (3) and (4) may be obtained at 25° C. from measurements of the electromotive force of the cell, $Ag/AgCl/HCl/H_2$, and is $\Delta F = -36{,}896$ cal.

The free energy increase of reaction (5) is calculable in a number of ways, for example, from the ionization constant of liquid water, as determined from conductivity measurements, or from the electromotive force of "acid-alkali" cells. The best data give $\Delta F_{25^\circ C.} = -38{,}210$ cal.

The free energy increase for reaction (6) is given from the equilibrium constant (vapor pressure) for the vaporization of water. At 25° C. we have $\Delta F = 2053$ cal.

Combining reactions 1–6, we have for reaction 183, $\Delta F_{25^\circ C.} = -2395 + 21{,}040 - 36{,}896 - 38{,}210 + 2053 = -54{,}408$ cal.

(*c*) Equation (183) may also be obtained by combining the following reactions:

$$\begin{aligned} (1) \quad & Hg(1) + \tfrac{1}{2}O_2 = HgO, \\ (2) \quad & H_2 + HgO = Hg(1) + H_2O(1), \\ (3) \quad & H_2O(1) = H_2O_{(gas)}. \end{aligned}$$

The equilibrium constant for the first reaction has been determined by direct measurement, at the boiling point of mercury, and, by extrapolation through equation (80), we obtain at 25°, $\Delta F = -13{,}786$ cal.

From measurements of the electromotive force of the cell,

$$Hg/HgO_{(s)}/KOH_{(aq)}/H_2,$$

the free energy increase at 25° C. of reaction (2) may be calculated to be $\Delta F = -42{,}752$.

Combining these values with that of (3) determined above, we have for reaction (183), $\Delta F_{25^\circ C.} = -13{,}786 - 42{,}752 + 2052 = -54{,}485$ cal.

(*d*) Equation (183) may also be obtained by combining

$$\begin{aligned} (1) \quad & H_2 + Cl_2 = 2HCl_{(aq)}, \\ (2) \quad & 2HCl_{(g)} + \tfrac{1}{2}O_2 = H_2O_{(gas)} + Cl_2, \\ (3) \quad & 2HCl_{(aq)} = 2HCl_{(g)}. \end{aligned}$$

The free energy increase for reaction (1) may be calculated from measurement of the electromotive force of various cells, and is $\Delta F_{25^\circ C.} = -62{,}734$ cal.

The free energy increase for reaction (2) may be calculated from direct measurements of the equilibrium constant for the reaction, which by extrapolation to 25° C. give $\Delta F_{25^\circ C.} = -9120$ cal.

The free energy increase for reaction (3) may be obtained from equilibrium (vapor pressure) measurements of hydrochloric acid solutions:

$$\Delta F_{25^\circ C.} = +17{,}350 \text{ cal.}$$

Combining these data, we obtain for reaction (183),

$$\Delta F_{25^\circ C.} = -62{,}734 - 9120 + 17{,}350 = -54{,}504 \text{ cal.}$$

Finally, it is possible, through the third law of thermodynamics (see Chapter XVII), to calculate the free energy increase for reaction (183) from the entropies of hydrogen, oxygen and water, employing equation (182). The entropy change for the reaction, ΔS, is equal to $S_{H_2O} - S_{H_2} - \frac{1}{2}S_{O_2}$. The entropies of hydrogen and oxygen are known with a fair degree of certainty from measure-

ments of the heat capacities of these substances at very low temperatures, and from theoretical considerations. The entropy of liquid water, from heat capacity data alone, is known only approximately,[1] but it may serve for a rough calculation, merely to illustrate the method of calculation. The best values, at 25° C., are

$$S_{H_2} = 29.44 \text{ cal./degree},$$
$$\tfrac{1}{2}S_{O_2} = 24.0 \quad \text{“} \quad ,$$
$$S_{H_2O(l)} = 16.8 \quad \text{“} \quad .$$

ΔS, therefore, for the formation of liquid water at 25° C. $= +16.8 - 29.44 - 24.0 = -36.64$ cal./degree.

For the heat of reaction at 25° C., $\Delta H = -68{,}270$ cal., whence, by equation (182),

$$\Delta F - \Delta H = -T\Delta S,$$
$$\Delta F_{25^\circ C.} = -57{,}391 \text{ cal.}$$

Combining this value with the free energy of vaporization ($\Delta F = 2035$), we obtain for equation (183), $\Delta F = -55{,}318$ cal.

It has thus been possible to calculate the free energy change for the formation of one mol. of gaseous water from its elements at 25° C. and atmospheric pressure by five methods, involving a wide range of experimental method and data from a variety of sources. The results may be repeated as follows:

(*a*) $\Delta F = -54{,}590$ cal.,
(*b*) $\Delta F = -54{,}408$ “ ,
(*c*) $\Delta F = -54{,}485$ “ ,
(*d*) $\Delta F = -54{,}504$ “ ,
(*e*) $\Delta F = -55{,}318$ “ .

If the mean of these values, or preferably the most probable value based upon the certainty with which the particular experimental data are known, be taken, and combined with the values for the heat of the reaction and the heat capacities of hydrogen, oxygen and water, we may by equation (80) express ΔF as a function of temperature (see Chapter II) which will permit the calculation of the equilibrium constant and hence the equilibrium concentrations for any desired conditions of temperature, pressure, or proportions or reactants.

This reaction has been discussed at length because it illustrates extremely well the value of an exact knowledge of the free energy change in reactions, and the methods by which equilibrium calculations may be made through a study of these free energy increases. If the free energy increase of formation of all chemical compounds were available, it would be possible, theoretically, to calculate the equilibrium constants for any reaction which one might choose to write, whether or not such reaction were experimentally feasible. It is all too frequently true that experimental data are unavailable or uncertain in particular cases. This only emphasizes the need for systematic investigations in this direction, and for an exact understanding of the factors involved in chemical equilibrium.

[1] Lewis and Gibson, *J. Am. Chem. Soc.*, 39, 2554 (1917).

CHAPTER IX

HETEROGENEOUS EQUILIBRIUM

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Any system composed of two or more phases may be the seat of heterogeneous equilibria as well as of homogeneous equilibria. Where the chemical or physical reactions which have reached a condition of equilibrium are wholly confined to a single phase, the equilibrium is regarded as homogeneous; such would be the equilibrium between the dissolved molecules of sodium chloride and the ions which they form. When however the reactions which occur involve a movement of substance from one phase to another, the equilibrium attained is spoken of as heterogeneous; such equilibria exist for example in the evaporation and condensation of water, or in the dissolving and precipitation of a solid salt in water.

It is quite obvious that heterogeneous equilibria can not be more simple than those occurring in homogeneous systems; indeed, they may frequently be much more complex. In some cases the equilibria are greatly affected by the surface conditions at the interface between the phases; such cases are dealt with in the chapter on colloid chemistry. In the present chapter the discussion will be restricted to those cases of heterogeneous equilibria in which only temperature, pressure and concentration are effectual influences. For these cases there are known two fundamental principles which are sufficient for systematizing practically all the phenomena; these principles are known as the Distribution Law and the Phase Rule. The former of these, which will be studied first, is quantitative in nature and, within certain limits, is of very great value in defining heterogeneous equilibria; the latter and broader principle will be studied at a later point in the chapter.

THE DISTRIBUTION LAW

The distribution law expresses a mathematically constant ratio between the concentrations of a given molecular species in any two phases of a system at constant temperature. It expresses the ratio equally well whatever possible combination of gaseous, liquid or solid phases is under observation. It has however required a long period of time for this entirely general form of the law to be recognized; initially only special combinations of phases were known to fall within its scope. The first statement of the law, covering only the equilibrium between a gas and its solution in a liquid, was made by William

Henry,[1] and is commonly referred to as Henry's law. At a later date, Berthelot and Jungfleisch [2] studied the partition of iodine between carbon disulphide and water, and stated the applicability of the principle to the distribution of a dissolved body between two liquid phases. Nernst,[3] studying distribution in systems of the same type (liquid-liquid), added the important restriction that a constancy in the distribution ratio can exist only between those molecules of the distributed substance which are in the same condition in both phases, pointing out that no immediate equilibrium and hence no immediate distribution can occur between simple molecules in one phase and associated molecules in a second phase, or between simple molecules and their dissociation products in different phases.

Distribution in the System Gas-Liquid

The equilibrium existing between a gas and its solution in a liquid is found to follow the law of Henry, who was the first to observe the simple relationship which exists. Henry's law may be stated as follows: the mass of a gas absorbed or dissolved by a given volume of a liquid is proportional to the pressure of the gas, at constant temperature. A simple algebraic statement of the law takes the form

$$\frac{m}{p} = K_1,$$

where m is the mass absorbed and p the pressure of the gas. This equation is easily changed so as to show the volume of the gas absorbed instead of its mass. The mass is proportional to the volume, by Avogadro's hypothesis, and is likewise proportional to the pressure, by Boyle's law; i.e., $m = pvK'$. If this value be substituted for m in the first equation, it becomes

$$v = \frac{K_1}{K'} = K_2;$$

that is, the volume of gas absorbed is independent of the pressure. Still a third form may be derived from the first; if mass m of the gas be absorbed in unit volume of the liquid, the amount present constitutes the concentration in the liquid phase and may be written C_2; in the gaseous phase the concentration C_1 is proportional to the pressure; introducing these values for m and p in the equation and inverting,

$$\frac{C_1}{C_2} = K_3.$$

This is the most generalized expression for Henry's law, and is likewise a direct algebraic statement of the distribution law, namely, that *the concentrations of*

[1] *Phil. Trans.* (1803); *Gilbert's Annalen*, **20**, 147 (1805).
[2] Berthelot and Jungfleisch, *Ann. chim. phys.*, (4) **26**, 396 (1872).
[3] Nernst, *Z. physik. Chem.*, **8**, 110 (1891).

any single molecular species in two phases at equilibrium bear a constant ratio to each other, the temperature remaining constant.

Henry's law may be predicted qualitatively from the theorem of Le Chatelier, which is of the broadest applicability. According to this theorem a system at equilibrium, if subjected to a stress, will undergo a change of equilibrium tending to reduce the intensity of the stress. Obviously the pressure exerted upon a gas will be reduced by any change which reduces the volume. Since the solution of a gas always produces a reduction in the total volume of a system, it follows that an increased solubility of gas will result from an increase of pressure, which is a qualitative statement of Henry's law.

One of the early applications of Henry's law was made by Dalton [1] in the experimentation on which his well-known law of partial pressures is based. Dalton deduced from his experiments that in a mixture of gases the absorption of each by a liquid is proportional to its own pressure, and not to the total pressure. It is thus shown that Henry's law applies to each component of a mixture of gases as well as to a single gas.

The experiments of Bunsen [2] subjected the law of Henry to a fairly rigorous test. Bunsen determined the weight of carbon dioxide gas dissolved by a fixed quantity of water at a number of pressures, all less than one atmosphere. In Table I, which includes some of Bunsen's results, the column headed P gives the experimental pressures in meters of mercury and g the weight of gas dissolved by a fixed volume of water.

TABLE I

Solubility of CO_2 in Water

Temperature	No.	P	g	P/P_1	g/g_1
19.9° C.	1	0.7255	38.61	—	—
"	2	0.5245	27.24	1.38	1.42
"	3	0.5237	27.08	1.39	1.43
"	4	0.5231	27.28	1.39	1.42
3.2°	1	0.5244	31.41	—	—
"	2	0.6467	38.66	0.8109	0.8125
"	3	0.6470	38.49	0.8109	0.8161

Taking the results at a fixed temperature, as at 19.9° C., the pressures of experiments 2, 3 and 4 are compared with those of experiment 1, giving the ratio P/P_1, and in like manner the ratio g/g_1 is that of the weights absorbed. Strict compliance with Henry's law would require that the ratios have the same value; the agreement is not perfect, but within the probable experimental error. Further experiments by Bunsen, by Khanikow and Luganin,[3] and by others,[4] together with the early work of Henry and of Dalton, have established that, for moderate pressures, the law of Henry holds with at most small variation.

Notwithstanding this satisfactory condition, there have been numerous cases where experimental results and the requirements of Henry's law diverge greatly. These deviations fall into two principal classes. Many of the apparent discrepancies are due to the application of the law without reference to the important restrictions pointed out by Nernst (*loc. cit.*), and can be brought into harmony by comparatively simple mathematical correction;

[1] *Memoirs Literary and Phil. Soc. of Manchester*, **1**, 1805; *Gilbert's Annalen*, **28**, 397 (1808).
[2] Bunsen, *Ann.*, **93**, 1 (1855).
[3] *Ann. chim. phys.*, (4) **11**, 412 (1867).
[4] Ostwald, *Lehrbuch*, I, 620 (Leipzig, 1903).

other cases appear to be due to the condition of high concentration and indicate that Henry's law, like other gas laws, is strictly applicable only to ideally dilute gases and fails to represent the facts when the concentrations become large. Each of these types of deviation is worth careful study.

The fact that the unmodified law of Henry could not properly be applied to cases where chemical action occurs between the gas and liquid was recognized by Bunsen (*loc. cit.*) and was doubtless in the mind of all careful workers in the field. It remained for Nernst (*loc. cit.*) to state in more precise terms what was hinted at in the vaguely used phrase, chemical action; and although Nernst's argument was developed for systems of two liquids, it applies just as logically where the gaseous phase is concerned. Nernst shows that we cannot logically think of a substance as distributed between two phases if its molecular condition in the two phases is different; for example, double molecules, formed by association in one phase, cannot be in immediate equilibrium with unassociated molecules in a second phase. If however the associated molecules in the first phase undergo reversible dissociation so that an equilibrium between associated and unassociated molecules exists in that phase, then an equilibrium will exist between the unassociated molecules in the two phases. The constant ratio of concentrations should be found, therefore, not between the total con centrations in the two phases, but between the concentrations of that molecular species which is common to both phases. Such an equilibrium can be illustrated by the following scheme, in which xy represents the simple molecules and $(xy)_n$ the associated molecules:

$$\begin{array}{rl} \text{gaseous phase:} & xy \\ & \downuparrows \\ \text{liquid phase:} & n \cdot xy \rightleftharpoons (xy)_n. \end{array}$$

If the substance in the liquid phase undergoes direct combination with the solvent, which will be represented by S, the diagram becomes

$$\begin{array}{rl} \text{gaseous phase:} & xy \\ & \downuparrows \\ \text{liquid phase:} & xy + nS \rightleftharpoons xy \cdot nS. \end{array}$$

A further possibility is that of dissociation, either electrolytic or non-electrolytic:

$$\begin{array}{rl} \text{gaseous phase:} & xy \\ & \downuparrows \\ \text{liquid phase:} & xy \rightleftharpoons \overset{+}{x} + \overline{y}. \end{array}$$

In addition to these three possibilities, cases will frequently occur in which any two or even three of these equilibria are met in the liquid phase. It is clear that if Henry's law is to be evaluated for any such instances, the constants for these homogeneous equilibria must be known, so that the true concentration of the distributed substance in each phase may be calculated from the total concentration present.

The case in which combination occurs between the distributed substance and the solvent, as indicated in the second scheme above, is actually freer from complications than might appear. In such an instance, Henry's law is applied to the distribution equilibrium and the mass law is applied to the reaction occurring in the liquid phase between the distributed molecules and the solvent. If now

C_1 = concentration of distributed molecules in the gaseous phase,
C_2 = concentration of distributed molecules in the liquid phase,
C_s = concentration of solvent molecules,
C_c = concentration of compound molecules,

the two laws may be written as follows:

$$\frac{C_1}{C_2} = K \text{ (Henry's law);} \tag{1}$$

$$\frac{C_2 \times (C_s)^n}{C_c} = K_1 \text{ (law of mass action).} \tag{2}$$

The concentration of solvent molecules C_s is very large and does not vary appreciably in dilute solution; $(C_s)^n$ may therefore be written as a constant and the law of mass action becomes

$$\frac{C_2}{C_c} = K_2. \tag{3}$$

Combining equations (1) and (3), the complete equation becomes

$$\frac{C_1}{C_2 + C_c} = K_3.^1 \tag{4}$$

It is thus shown that Henry's law may be tested according to equation (4), in which the sum $C_2 + C_c$ is the *total* concentration of the gas in the liquid phase as it would be ordinarily determined by analysis. The occurrence of compound formation therefore will have no influence upon Henry's law except as to the numerical value of the constant.

The case is quite different however if association or dissociation occur; it then becomes necessary to take the extent of these changes into account. The algebraical treatment again is based upon the use of the mass law to ex-

[1] The algebraic derivation is as follows: by inversion of equation (3),

$$\frac{C_c}{C_2} = \frac{1}{K_2},$$

whence

$$\frac{C_c + C_2}{C_2} = \frac{1 + K_2}{K_2}$$

divided into equation (1),

$$\frac{C_1}{C_2 + C_c} = \frac{KK_2}{1 + K_2} = K_3.$$

press the degree of dissociation or association. Let C now stand for the total concentration in the liquid phase as a alytically determined, and α stand for the degree of dissociation; then the mass law expression will be, for a binary electrolyte,

$$\frac{(C\alpha)^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} = K_m,$$

whence

$$\alpha = \frac{-K_m + \sqrt{K_m^2 + 4K_mC}}{2C}.$$

Writing Henry's law in the same terms as before, and remembering that C_2, the concentration of undissociated molecules in the liquid phase, is equal to the fraction $(1-\alpha)$ of the total concentration C,

$$K = \frac{C_1}{C_2} = \frac{C_1}{C(1-\alpha)} = \frac{2C_1}{2C + K_m - \sqrt{K_m^2 + 4K_mC}}.$$

Henry's law may therefore be tested for a compound which undergoes dissociation (electrolytic or non-electrolytic) by analysis of the gaseous and liquid phase, if the dissociation constant K_m is also known and the total concentrations in the two phases, C and C_1, be determined.

The solubility of ammonia in water may be studied according to this method. The equilibria here are as follows:

gaseous phase: NH_3

$$\updownarrow$$

liquid phase: $NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows \overset{+}{N}H_4 + \overset{-}{O}H.$

Here the formation of the compound NH_4OH is without effect on the form of the equations, as shown above, and the dissociation constant is known. Calingaert and Huggins[1] have tested dilute solutions of ammonia from a concentration of 1.25 gms. to .005 gm. per liter at 100°. The column headed C in Table II gives the tctal concentration in the liquid phase, in gms. per liter of solution, the column C_1/C the experimentally found ratio in the two phases, $1-\alpha$ the undissociated fraction of the ammonium hydroxide in the liquid phase, and k the constant for Henry's law, obtained by the equation $k = C_1/C(1-\alpha)$.

TABLE II

AMMONIA AND WATER AT 100°

C	$K = \frac{C_1}{C}$	$1-\alpha$	$k = \frac{C_1}{C(1-\alpha)}$
1.256	12.92	0.987	13.1
0.633	12.67	0.981	12.9
0.305	12.44	0.973	12.8
0.148	12.13	0.963	12.6
0.0386	12.06	0.926	13.0
0.0190	11.83	0.896	13.2
0.0107	11.53	0.864	13.3
0.0046	11.05	0.806	13.6

[1] *J. Am. Chem. Soc.*, 45, 915 (1923).

It is apparent that, when the dissociation is ignored, as in column 2, the quotient shows a regularly diminishing value, but, when the correction for dissociation is introduced, as in column 4, there is a satisfactory constancy. The solutions are all, it will be noted, very dilute, and the gas pressure correspondingly low.

When the gas pressures used are large, deviations from Henry's law are found which cannot be compensated for by assuming polymerization or dissociation. Deviations of this sort were noted by Roscoe and Ditmar [1] and by Sims.[2] When the pressures are no larger than one or two atmospheres, variations of considerable magnitude appear. The variation was found to be dependent also on the temperature; thus, at 0°, the solubility of ammonia in water fails to follow the law, while at higher temperatures a much closer approximation to the law is obtained. Although the correction for electrolytic dissociation of the ammonia has not been applied here, such a correction would have no important effect, as the dissociation is extremely small at these concentrations. The results are shown graphically in Fig. 1. A straight line in each case gives the ideal curve; its slope is fixed by the position of the point *b*, which is taken from the observed data at 76 cm. pressure. At 0°, the curve for the absorption of ammonia shows that the absorption is greater than calculated by the law when the pressures are low, but is less than the requirement at higher pressures. The isothermal curves at 20°, 40° and 100° indicate that as the temperature rises the absorption approaches more nearly the theoretical, the pressures still being low.

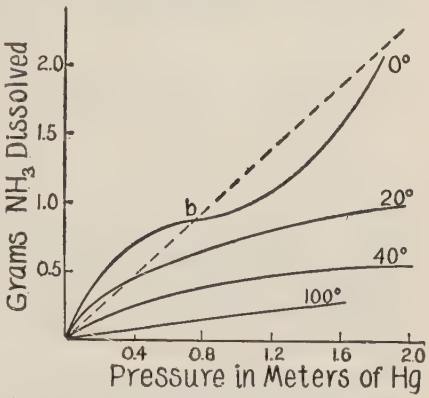


Fig. 1. Solubility of Ammonia at Varying Temperatures and Pressures

Extensive experimentation by Sander [3] has shown still greater deviations from the law when the pressures are high. The absorption of carbon dioxide in water, alcohols, ether, aromatic hydrocarbons and other organic solvents led to the following conclusions. The solubility of carbon dioxide at pressures of 20 to 140 kg. per square centimeter varies from Henry's law at low temperatures, but approaches the required values at higher temperatures; at 100° the solubility is proportional to the pressure within the experimental error. With respect to the extent of deviation at low temperatures, it is less in water, and greater in all the organic solvents; this comparison makes it clear that the deviations are not caused by electrolytic dissociation, whether or not association plays a part. As a correction of interest, it is found that a closer approximation to Henry's law is found if the weight of absorbed gas is referred to the volume of the solution rather than to that of the pure solvent.

The above variations observed by Sander occur when the concentration in the gaseous phase is very high, under which condition the general equation of state for a gas, $PV = RT$, is likewise known to fail. The question arises whether high concentrations in the liquid

[1] Roscoe and Ditmar, *Ann.*, **112**, 349 (1859).
[2] *Ann.*, **118**, 345 (1861).
[3] Sander, *Z. physik. Chem.*, **78**, 513 (1912).

phase bring about a similar result. The experiments of Sackur [1] appear to answer that question in the negative, at least for the gas carbon dioxide in several organic liquids. Sackur selected methyl alcohol, ethyl alcohol, acetone, methyl acetate and ethyl acetate for solvents at very low temperatures, under which conditions the solubility is very high while the vapor pressure of the gas is low. The results of his experiments are given in part in Table III. The figures under P represent the pressure of the gaseous phase in mm. of mercury, those under K the constant for Henry's law, but with the terms in such order that the ratio is that of the concentration in the liquid phase to that in the gaseous phase.

TABLE III

Solubility of Carbon Dioxide in Methyl Alcohol

P	K at $-78°$	K at $-59°$
50	120.5	—
100	119.6	42.5
200	120.1	42.7
400	122.2	43.1
700	126.8	—
740	—	43.3

The values of the constant show but slight variation through a considerable range, indicating that up to high concentrations in the liquid phase there is little modification of the law necessary; the variation in the case of the other solvents is slightly greater. When the constant is calculated on the basis of mass of gas absorbed per unit volume of solvent instead of solution, the variation is much greater, which result is in accord with that already noted by Sander (*loc. cit.*).

The solubility of hydrogen chloride in water is an interesting case of an exception to Henry's law. Roscoe and Ditmar (*loc. cit.*) have investigated the dependence of this solubility upon the pressure. Since the compound is a strong electrolyte, it is apparent that a correction of very large magnitude must be made if the law is to have a proper test, and this has not yet been done. It appears from the experiments however that the gas has a very considerable solubility in water even when the pressure has become too low to be measurable. Ostwald [2] interprets this result, through graphic extrapolation of the solubility curve, to mean that there is a residual solubility which is independent of the pressure, but varying in composition with the temperature. This is in agreement with the experiments of Richards and Singer,[3] who found that a tenth-normal solution of hydrochloric acid emits only a negligible amount of acid upon prolonged boiling.

A survey of these and similar investigations leads to the general conclusion that Henry's law, like other gas laws, is strictly applicable only to ideal gases, and fails to express exact relations as the gas departs from ideal conditions.

The foregoing discussion of Henry's law has been based upon the absorption of the gas at constant temperature. A question naturally arises as to the change in value of these absorption coefficients with change of temperature. But little of an entirely general character has been learned. There is, of course, no doubt that van't Hoff's law of mobile equilibrium applies here; if the temper-

[1] Z. *Elektrochem.*, **18**, 641 (1912).
[2] Ostwald, *Lehrbuch*, **I**, 623. Leipzig, 1903.
[3] *Am. Chem. J.*, **27**, 208 (1902).

ature of a system at equilibrium is raised, that reaction occurs which is accompanied by the absorption of heat, i.e., the endothermal reaction. If it is known therefore that the process of solution of a gas, at the equilibrium concentration, is an endothermal change, it follows qualitatively that the solubility of that gas will increase with increasing temperature, and in cases where solution is exothermal the reverse will be true. It is an empirical fact that the dissolving of a gas is an exothermal process in the majority of cases, whence it follows that the solubility decreases with the temperature; in such cases, the constants of Henry's law will then show a changing value with increase of temperature, or, to phrase the same relation otherwise, the gas will have a negative solubility coefficient. But this is by no means always the case; the temperature coefficient is found to be positive in some instances, and in a few cases passes from a positive through a zero value to a negative value as the temperature changes. A few instances will show that all such are possible.

Bunsen (*loc. cit.*) believed that hydrogen in water and also oxygen and carbon monoxide in alcohol all have a zero temperature coefficient; Winkler and Bohr [1] find however that hydrogen has a negative coefficient at low temperatures, passing through a zero value at about 60° and having a positive value above that temperature. Just [2] has made an extensive study of the solubility of nitrogen, hydrogen and carbon monoxide in water and in a large number of organic solvents, at 20° and 25°; the temperature coefficient is positive in all solvents except water. For carbon dioxide, on the other hand, Sander (*loc. cit.*) finds a negative coefficient in all solvents, with nitrobenzene as a possible exception. Geffken's [3] figures for the solubility of carbon dioxide in water may be regarded as a fairly typical case; the temperature coefficient is negative, as shown in Table IV, where the Bunsen absorption coefficient is indicated by the values of β at different temperatures; it is defined as the volume of gas, measured under standard conditions, absorbed by unit volume of solvent.

TABLE IV

Solubility of Carbon Dioxide in Water

Temperature	β	Temperature	β
0	1.713	25	0.759
5	1.424	30	0.665
10	1.194	40	0.530
15	1.019	50	0.436
20	0.878	60	0.359

The distribution law can be applied to simpler systems of gases and liquids than those discussed above, namely, to systems consisting of a single liquid and its vapor. At a constant temperature the ratio of concentrations in the two phases should be constant, which is equivalent to the statement that a pure liquid has a single fixed vapor pressure. If one considers the possibility of a pressure change, it appears that it has little effect upon the concentration of the liquid phase within reasonable limits, since the compressibility of liquids is of exceedingly small magnitude; the concentration in the liquid phase being therefore practically constant, the distribution law indicates that the concentration in the gaseous phase will likewise remain substantially unchanged. If a higher total pressure is put upon the system through the agency

[1] *Wied. Ann.*, 62, 644 (1897).
[2] *Z. physik. Chem.*, 37, 342 (1901).
[3] *Z. physik. Chem.*, 49, 271 (1904).

of some second gas which is introduced, the pressure of the distributed phase (i.e., the vapor of the liquid) will vary but slightly. The *exact* relationship which exists between the vapor pressure exerted by a liquid and the applied external pressure has already been given in Chapter IV, page 120.

Not only may the vapor tension of a pure liquid be shown to be a constant by application of the distribution law, but it is also possible by the same means to arrive at a derivation of Raoult's law, which expresses the depression of vapor pressure of a solvent upon addition of a solute. Let N equal the number of mols. of pure solvent taken for consideration, to which n mols. of solute are added; the molar concentration of solvent then falls from N/N to $N/(N+n)$. The distribution law requires however that the ratio of concentrations of the solvent in the gaseous and liquid phases remain constant; whence, writing C_0 and C as the concentrations of solvents in the two gaseous phases,

$$\frac{C_0}{N/N} = \frac{C}{N/(N+n)},$$

$$\frac{C_0}{C} = \frac{N+n}{N},$$

$$\frac{C_0 - C}{C_0} = \frac{n}{N+n},$$

Since the pressures in the gaseous phases are proportional to the concentrations, and representing these pressures by p_0 and p,

$$\frac{p_0 - p}{p_0} = \frac{n}{N+n},$$

which is the familiar form of Raoult's law for ideal solutions.[1]

Distribution in the System Liquid-Liquid

The distribution law has had its principal test in the case of liquid-liquid systems; furthermore, the application of the law to such systems has yielded most interesting and useful results and made possible the interpretation of a large number of otherwise inexplicable facts. Berthelot and Jungfleisch (p. 344, *loc. cit.*) were the first to make a systematic investigation of systems of this sort and to note the general underlying law. The following table (Table V) gives some of their experimental results.

Inspection of the values of K in these tables shows that constancy in an exact sense is not attained, which fact was not overlooked by the experimenters themselves; but the approximation to constancy in these cases, in which the actual concentrations are varied considerably, is sufficient to indicate the underlying principle. In the case of the two acids no consideration of dissociation was taken into account, as the work antedated the dissociation theory. Other cases of distribution between two liquids have been studied in large number,[2] and in the majority of cases considerations of dissociation or association are necessary before the constancy of ratio can be detected; but, it is also true that, in addition to the cases of iodine and bromine in carbon disulphide and water as tabulated by Berthelot and Jungfleisch, there is a considerable number of

[1] For a discussion of Raoult's law, see Kendall, *J. Am. Chem. Soc.*, **43**, 1391 (1921).

[2] See Herz, *Der Verteilungssatz*, Stuttgart, 1909.

TABLE V

DISTRIBUTION OF SOLUTE BETWEEN TWO LIQUIDS

Iodine in Carbon Disulfide and Water at 18°			Bromine in Carbon Disulfide and Water at 20°		
Gms. I per 10 cc. H_2O	Gms. I per 10 cc. CS_2	$K = \frac{C_1}{C_2}$	Gms. Br per 10 cc. H_2O	Gms. Br per 10 cc. CS_2	$K = \frac{C_1}{C_2}$
0.0041	1.74	420	0.176	10.2	58
0.0032	1.29	400	0.030	2.46	82
0.0016	0.66	410	0.020	1.55	78
0.0010	0.41	410	0.0011	0.09	80
0.00017	0.076	440			

Succinic Acid in Ether and Water at 15°			Oxalic Acid in Ether and Water at 11°		
Gms. Acid per 10 cc. H_2O	Gms. Acid per 10 cc. Ether	$K = \frac{C_1}{C_2}$	Gms. Acid per 10 cc. H_2O	Gms. Acid per 10 cc. Ether	$K = \frac{C_1}{C_2}$
0.486	0.073	6.6	0.473	0.052	9.0
0.420	0.067	6.3	0.436	0.046	9.5
0.365	0.061	6.0	0.304	0.031	9.8
0.236	0.041	5.7	0.203	0.0205	9.9
0.121	0.022	5.4			
0.070	0.013	5.2			
0.024	0.0046	5.2			

other instances in which the uncorrected ratio in two liquids, as determined by analysis, is reasonably constant over quite large variations in the actual concentrations. Such cases include hydrogen peroxide [1] in water and various organic liquids, boric [2] acid in water and amyl alcohol, bromine [3] in water and bromoform, iodine [3] in water and chloroform and in water and ethylene glycol, and phenol [4] in water and amyl alcohol.

If a true constancy in the value of K is assumed for a simple case of distribution between two liquids, as in the instances referred to, an interesting corollary follows. The addition of a larger total quantity of solute will not alter the ratio of concentrations in the two layers, and the process may be imagined as continued until one of the phases is saturated with respect to the solute. The question arises as to the effect of further addition of solute. It

[1] Calvert, *Z. physik. Chem.*, **38**, 513 (1901); Walton and Lewis, *J. Am. Chem. Soc.*, **38**, 633 (1916).

[2] Abegg, Fox and Herz, *Z. anorg. Chem.*, **35**, 129 (1903).

[3] Jakowkin, *Z. physik. Chem.*, **18**, 585 (1895).

[4] Herz and Fischer, *Ber.*, **37**, 4746 (1904); **38**, 1138 (1905); Landau, *Z. physik. Chem.*, **73**, 200 (1910).

cannot enter the phase assumed to be saturated, by definition of the term; nor can it enter the other phase by the assumption of the distribution law, since its further solution would alter the value of the constant. It follows then that both phases are saturated with respect to the solid and that the distribution ratio is the ratio of the solubilities of the solute in the two solvents. From this process of reasoning it results that the distribution law is frequently so phrased as to state that the distribution ratio of a solute between two solvents is the ratio of its solubilities in the two solvents. This is of course an entirely logical statement on the assumption that no correction factors are necessary; but, as a matter of fact, no data have yet been assembled which support this simple statement, and it is probable that it is true only for the distribution of very insoluble substances; for, it will be shown that, in the case of liquid systems, as it has already been shown for the system gas-liquid, the distribution law is strictly applicable only to ideally dilute solutions.

If the distribution ratio is to be constant in systems consisting of two liquids, there is another assumption that must be made, namely, that the two liquids are mutually insoluble, or, at any rate, do not have their mutual solubility altered by the presence of the distributed substance. In actual experimentation this condition has not been and probably cannot ever be strictly realized; actually the distributed substance does have an effect upon the mutual solubility, and that effect may vary both in amount and in direction. The distributed phase may lower the mutual solubility; in such a case it is conceivable that the mutual solubility might be reduced to zero by successive additions of solute, so that the limiting distribution ratio would be that of the solubilities in the pure solvent. The solubility of one liquid in the second may increase and that of the second in the first decrease by the addition of solute; in this case it is clear that the distribution ratio must vary throughout the whole range of concentrations. The third possibility is that the mutual solubilities of the two solvents are increased by addition of the solute; this will bring about a most interesting condition which will be more fully discussed from the standpoint of the phase rule under three-component systems. The obvious result of adding more and more solute in such an instance is to make the two liquid phases more and more like each other in composition until they become identical and dissolve in each other in all proportions. At this consolute concentration the ratio of the distributed compound in the two phases must be unity, as was pointed out by Klobbie [1] in the case of malonic acid dissolved in water and ether. There will in such cases be a variation of the ratio from whatever value it has in dilute solution to unity at the consolute concentrations, provided only that the liquid phases continue to dissolve the solute up to this point of complete mutual solubility. Any one of these three possibilities discussed above may be realized experimentally, and it is apparent therefore that the assumption of complete insolubility of the two liquids is, in the nature of things, not realizable when a third substance is added. If, however, the concentrations of the third substance are kept sufficiently small, this effect may be of

[1] *Z. physik. Chem.*, **24**, 629 (1907).

negligible dimensions; it appears therefore that, for liquid-liquid systems, as well as for gas-liquid systems, the distribution law may be applied successfully only when the solutions are dilute. It will be seen in the examples given that this requirement has been kept in mind when success has been attained.

Correction for Dissociation and Association. It has already been pointed out, in the discussion of Henry's law, that corrections for dissociation and association are necessary where these phenomena occur; the additional complication in liquid-liquid systems is that these corrections may be found necessary for both phases. Nernst (*loc. cit.*) modified the distribution law so as to make it applicable to such systems, stating the conditions as follows:

1. If the dissolved substance has the same molecular weight in both solvents, it possesses a distribution coefficient independent of the concentration, and vice versa.
2. If the dissolved substance consists of molecules of different weight or composition, the above first rule holds for each molecular species.

It has been pointed out in the discussion of Henry's law that, in the phase in which dissociation occurs, the total concentration, as determined analytically, is to be multiplied by the term $(1 - \alpha)$ before insertion in the distribution formula, where α is the fractional dissociation. It now remains to be shown how cases may be treated where the disturbing condition is that of association. Reference to Fig. 2 will indicate the proper method of reasoning. Let X represent the molecular species common to both liquid phases, and let it be associated in one phase to form double molecules, indicated as $(X)_2$. Analysis of the phase marked I gives us the concentration of X in that phase, represented by C; but analysis of phase II gives, not the concentration of X, which is necessary for testing the distribution law, but a concentration C_1 made up from both associated and non-associated molecules. The necessary term may be derived however by the application of the mass law to the equilibrium occurring in phase II. If α be the fractional dissociation into simple molecules, then

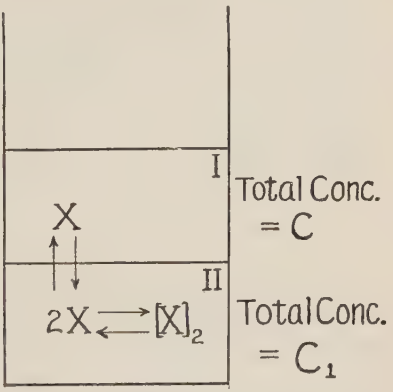


Fig. 2. Distribution Diagram for an Associated Compound

$$\frac{(C_1\alpha)^2}{C_1(1-\alpha)} = K, \qquad C_1\alpha = \sqrt{C_1(1-\alpha)K}.$$

Now $C_1\alpha$ is the concentration of simple molecules, and may be inserted in the distribution ratio:

$$K = \frac{C}{C_1\alpha} = \frac{C}{\sqrt{C_1(1-\alpha)K}},$$

$$\frac{C}{\sqrt{C_1(1-\alpha)}} = K\sqrt{K} = K'.$$

It will be seen that if the association were into molecules three times the weight of the simplest molecule, the radical would become a cube root, and, in more general terms, for association into a molecule $(X)_n$ the denominator would become an nth root. Considering however only the simpler cases of dissociation of a binary compound and association into double molecules, the following general formulæ have been developed:

$$\left.\begin{array}{l}\text{Phase I, neither association nor dissociation,}\\ \text{Phase II, neither association nor dissociation,}\end{array}\right\}\ \frac{C}{C_1} = K;$$

$$\left.\begin{array}{l}\text{Phase I, dissociation occurring,}\\ \text{Phase II, no molecular change occurring,}\end{array}\right\}\ \frac{C(1-\alpha)}{C_1} = K;$$

$$\left.\begin{array}{l}\text{Phase I, no molecular change occurring,}\\ \text{Phase II, association occurring,}\end{array}\right\}\ \frac{C}{\sqrt{C_1(1-\alpha)}} = K;$$

$$\left.\begin{array}{l}\text{Phase I, dissociation occurring,}\\ \text{Phase II, association occurring,}\end{array}\right\}\ \frac{C(1-\alpha)}{\sqrt{C_1(1-\alpha')}} = K.$$

In these general formulæ, C and C_1 represent the concentrations as analytically determined, α and α' the degree of dissociation as determined by independent methods; and the further assumptions are included that the degree of dissociation follows the mass law and that the distributed species is the simple molecule.

In several of the cases to be discussed, an algebraic simplification is possible for cases where association occurs. In benzene and similar hydrocarbons it happens that association is frequently complete or nearly so; the value of α therefore becomes very small as compared with unity in the term $(1 - \alpha)$, and may be neglected, so that the ratio becomes

$$C/\sqrt{C_1} = K,$$

thus rendering unnecessary any quantitative knowledge of the association equilibrium.

Nernst's generalizations, which are included in the foregoing discussion, receive support from his own experiments and more particularly from those of Hendrixson.[1] In Table VI are given the data for one of a series of eight careful distribution experiments in cases involving both dissociation and association. The predictions of the theory are fulfilled if it can be shown that, assuming a constant distribution ratio for the simple molecules of benzoic acid between water and benzene, the degree of molecular dissociation in the benzene phase follows the mass law. For this discussion, let

C_1 = the total concentration in the aqueous phase,
C_2 = the total concentration in the benzene phase,
α = the degree of electrolytic dissociation in the water,
k = the distribution ratio of simple molecules between water and benzene,
m_1 = the concentration of simple molecules in the benzene,
K = the molecular dissociation constant in the benzene.

The constancy of the values of K is to be proved, and it is obvious that it is some function of the distribution constant k. Of the terms listed above,

[1] *Z. anorg. Chem.*, 13, 73 (1897).

C_1 and C_2 are determined by analysis of the two phases at various total concentrations; α may be calculated from the Ostwald mass law for the dissociation of benzoic acid in water, $\frac{\alpha^2}{(1-\alpha)V} = 0.00006$. The value of k, the distribution constant, is arrived at by the following reasoning; it is of course the ratio of the simple molecules in the two phases, whence $k = \frac{C_1(1-\alpha)}{m_1}$. The equation, however, includes both k and m_1 as unknown terms. Proceeding further, K, the molecular dissociation constant in the benzene phase, has its value expressed by the application of the mass law to the equilibrium $2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$, whence

$$K = \frac{(m_1)^2}{C_2 - m_1} = \frac{\left[\frac{C_1(1-\alpha)}{k}\right]^2}{C_2 - \frac{C_1(1-\alpha)}{k}} = \frac{[C_1(1-\alpha)]^2}{C_2k^2 - C_1k(1-\alpha)}.$$

Assuming now that the value K is a constant, values of C_1 and C_2 from two experiments (lines 1 and 7) of Table VI are inserted in the equation and the value of the distribution constant k is found to be 0.700.

With this known, the value of m_1, the concentration of simple molecules, can be calculated by the formula $\frac{C_1(1-\alpha)}{m_1} = k$, and the figures are given in column 5. Column 6 gives the concentration of double molecules $C_2 - m_1$, and column 7 gives the nearly constant values for K.

TABLE VI

DISTRIBUTION OF BENZOIC ACID BETWEEN WATER AND BENZENE AT 10°
$k = 0.700$

C_1	C_2	d	$C_1(1-\alpha)$	m_1	$C_2 - m_1$	$\frac{m_1^2}{C_2 - m_1} = K$
0.0429	0.1449	0.169	0.0357	0.0510	0.0939	0.0277
0.0562	0.2380	0.149	0.0474	0.0677	0.1703	0.0269
0.0823	0.4726	0.125	0.0720	0.1029	0.3697	0.0286
0.1124	0.8843	0.104	0.1007	0.1439	0.7404	0.0279
0.1780	2.1777	0.0866	0.1626	0.2323	1.9454	0.0277
0.2430	4.0544	0.0747	0.2249	0.3213	3.7331	0.0276
0.2817	5.4851	0.0695	0.2621	0.3743	5.1108	0.0274

The literature contains a very considerable number of cases like the above in which distribution experiments have been used to determine dissociation or association or both. Ordinarily, the degree of dissociation has been known through independent conductivity experiments, and the degree of association determined by application of the theory as given above. Thus, Hendrixson (*loc. cit.*) determined the association of benzoic acid and of salicylic

acid in benzene and in chloroform. Herz and Fischer [1] and Herz and Lewy [2] have determined the association of acetic acid and chloracetic acid in benzene, toluene, xylene, chloroform, bromoform, carbon disulfide and carbon tetrachloride, using water as the other solvent in each case. Donnan and Garner [3] by the same method found lithium chloride to exist chiefly as double molecules in amyl alcohol.

There have been numerous cases like the above in which distribution experiments have been of use in measuring, with considerable accuracy, the degree of association of certain compounds. The effort, on the other hand, to use the same method of experimentation so as to measure the degree of electrolytic dissociation, has been much less often made and, on the whole, with much less success. This has been due, in considerable part, to the fact that but few compounds are known which meet the requirement of being fairly strong electrolytes (salts, strong bases and acids) and of being at the same time soluble both in water, where the dissociation occurs, and in non-dissociating solvents like the hydrocarbons. There is the further difficulty that, where the above requirements are met, the compound is associated in the second solvent and its degree of association not known with sufficient accuracy to be set into the above formulæ with any great degree of confidence. Where such experiments have been possible, they have led to conclusions as to the degree of electrolytic dissociation which are out of harmony with the results obtained by other methods. Thus Rothmund and Drucker [4] used distribution experiments in investigating the electrolytic dissociation of picric acid in water by measuring its distribution between that solvent and benzene. Algebraic treatment similar to that given above showed that, on the assumption that the acid exists wholly in the form of double molecules when in benzene, its dissociation in water follows the mass law, or Ostwald dilution formula, the dissociation constant being 0.164. This conclusion stands in contradiction to the fact that strong acids do not follow the Ostwald formula, as far as evidence exists based upon their electrical conductivity; the contrary evidence of Rothmund and Drucker is of course weakened by the fact that an assumption as to the association in benzene is involved. Later experiments by Drucker,[5] where tribenzylmethylammonium salts were used, gave a much less satisfactory constant for the distribution ratio when the assumption was made that the electrolytic dissociation followed the Ostwald formula. More extreme results have been found by Schuncke,[6] who noted that hydrogen chloride leaves ether completely and passes wholly into water, and by Hill,[7] who studied the distribution of silver perchlorate between water and benzene, water and toluene, and water and aniline; the salt passes wholly into the water in the first two cases and wholly into the aniline in the third case. In all these cases it is clear that there

[1] *Ber.*, **38**, 1138 (1905).
[2] *Z. Elektrochem.*, **11**, 818 (1905).
[3] *J. Chem. Soc.*, **115**, 1325 (1919).
[4] *Z. physik. Chem.*, **46**, 826 (1903).
[5] *Z. Elektrochem.*, **18**, 562 (1912).
[6] *Z. physik. Chem.*, **14**, 331 (1894).
[7] *J. Am. Chem. Soc.*, **43**, 254 (1921); **46**, 1132 (1924).

can be no molecular species common to both phases; what the condition of the distributed compound may be in each phase is not easy to determine.

Study of Other Equilibria by Means of Distribution Experiments: It will be readily seen that distribution experiments may shed much light on a variety of other chemical equilibria as well as upon association or dissociation. If x in Fig. 3 represent a substance whose distribution coefficient between two phases can be determined, and if it is capable of entering into a reversible reaction with a second substance y in one of the phases, the constants of this second equilibrium can be easily evaluated from a series of distribution experiments; analysis of the upper phase for its content of x will give the concentration of uncombined x in the lower phase from the distribution ratio previously determined, and analysis of the lower phase for x will give its total concentration as x and xy, from which the concentration of xy follows; since the total concentration of y is the amount taken, and its proportion in xy follows from knowledge of the composition of that compound, the concentration of uncombined y is likewise known, and with x, y and xy known in the lower phase the constants of the equilibrium can be immediately calculated.

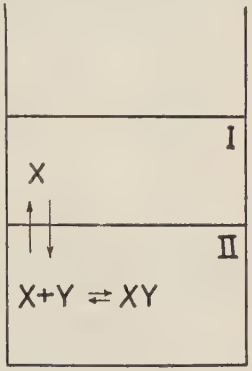


FIG. 3. Distribution Diagram for a Compound Undergoing Combination

In accordance with this principle, Kuriloff [1] has studied the equilibrium

$$\text{naphthol} + \text{picric acid} \rightleftharpoons \text{naphtholpicrate}$$

in benzene solution. Roloff [2] has studied the action of bromine on potassium bromide in forming the polybromide KBr_3, and Jakowkin [3] has studied the formation of similar polyiodides and the interesting case of the hydrolysis of chlorine:

$$Cl_2 + HOH \rightleftharpoons HCl + HClO.$$

Dawson [4] by studying the distribution of ammonia between chloroform and aqueous solutions of copper sulfate was able to show the existence of the compound $CuSO_4.4NH_3$ in the aqueous phase together with certain dissociation products. Farmer [5] has, in like manner, determined the hydrolysis of the barium salt of hydroxyazobenzene by distribution experiments between benzene and water. The method is one of very wide applicability, though it is unquestionably true that in many instances the conclusions are complicated by the fact that there are several equilibria occurring in each phase.

Nernst (*loc. cit.*) has given the most generalized form in which equilibria may be studied by means of distribution experiments. Let a two-phase system be considered, in each phase of which an equilibrium exists according to the following scheme:

$$n_1A_1 + n_2A_2 + \cdots \rightleftharpoons n_1'A_1' + n_2'A_2' + \cdots,$$

[1] *Z. physik. Chem.*, **25**, 419 (1898).
[2] *Z. physik. Chem.*, **13**, 341 (1894).
[3] *Z. physik. Chem.*, **20**, 19 (1896); **29**, 613 (1899); *Ber.*, **30**, 518 (1897).
[4] *J. Chem. Soc.*, **89**, 1666 (1906).
[5] *J. Chem. Soc.*, **79**, 863 (1901).

in which A_1, A_2, A_1' and A_2' represent molecular species and n_1, n_2, n_1' and n_2' represent the stoichiometrical coefficients; and let C_1, C_2, C_1' and C_2' represent the concentrations of these molecular species in the one phase at equilibrium, and c_1, c_2, c_1' and c_2' the concentrations in the second phase. The mass-law equations representing these equilibria in the two phases will be

$$\frac{C_1^{n_1}C_2^{n_2}}{C_1'^{n_1'}C_2'^{n_2'}} = K,$$

$$\frac{c_1^{n_1}c_2^{n_2}}{c_1'^{n_1'}c_2'^{n_2'}} = K_1.$$

Each of the molecular species is distributed between the two phases, which fact is represented by a series of distribution ratios

$$\frac{C_1}{c_1} = k_1, \quad \frac{C_2}{c_2} = k_2, \quad \frac{C_1'}{c_1'} = k_1', \quad \frac{C_2'}{c_2'} = k_2'.$$

By division of the first two equations, an equation results:

$$\frac{K}{K_1} = \frac{k_1^{n_1}k_2^{n_2}}{k_1'^{n_1'}k_2'^{n_2'}}.$$

It follows therefore that, if the equilibrium constants of a reaction occurring at a fixed temperature in a given phase are known and if, also, the distribution constants of all the molecular species are known, the equilibrium constant in the second phase at that temperature can be calculated. The conclusion is of course valid whether the two phases be liquids or whether one of them be a gaseous phase.

Amorphous Phases: The substitution of an amorphous body for one of the liquid phases should have no effect upon the validity of the distribution law. It is customary to look upon such amorphous bodies as liquids of high viscosity, which property should in no wise interfere with the establishment of a true equilibrium, although it may lengthen the time required for the attainment of equilibrium. Such a case has been studied by Küster;[1] ether distributes itself between water and the amorphous substance caoutchouc as shown in Table VIII.

The application of the distribution law to cases involving a colloidal substance is simple in principle, but the interpretation of the results is by no means simple. The adsorption of dissolved substances from solutions upon colloidal bodies is obviously a case of distribution of a substance between two phases. Indeed, a common method of writing the adsorption isotherm, $\frac{C^n}{C} = K$, is formally identical with the distribution law as it has been used for cases in-

[1] *Z. physik. Chem.*, **13**, 452 (1894).

TABLE VIII

DISTRIBUTION OF ETHER BETWEEN CAOUTCHOUC AND WATER AT 18°

C_k	C_w	C_k/C_w	$\sqrt{C_k}/C_w$
3.85	1.24	3.10	1.58
7.96	2.34	3.41	1.21
16.14	4.26	3.79	0.94
20.12	5.07	3.97	0.88
24.49	5.66	4.33	0.87
28.82	6.37	4.40	0.83
31.43	6.99	4.50	0.80
35.09	7.40	4.74	0.80
38.09	7.93	4.80	0.78
49.18	9.18	5.36	0.76

The first column indicates the grams of ether per 100 cc. of the caoutchouc phase and the second column the number of grams in the same volume of the aqueous solution. The ratio of these values, given in column three, gives figures with a decided trend, but the substitution of the square root of the values of C_k in the formula (Column 4) gives values which are not far from a constant; the conclusion is therefore that, in the caoutchouc phase, the ether is predominatingly bimolecular.

volving association; but where adsorption from water occurs, for example, the exponent n must be applied to the *water* phase, and is of the order of magnitude of 1/5 or 1/10. Reasoning such as has been used in distribution experiments would therefore lead to the astounding conclusion that the distributed phase has only a fraction of the molecular weight in the colloid which it possesses in water. Since compounds usually possess their minimum molecular weight in water, the conclusion that they have still lower molecular weights in the colloid phase is untenable; rather, it seems wiser to conclude that surface effects have here a predominating influence because of the huge surfaces possessed by colloids, and that the distribution law is masked by these greater influences.

The Process of Extraction: Probably the commonest use to which the distribution principle is put in ordinary laboratory practice is the process of extraction. Organic compounds in particular are easily and completely removed from inorganic materials by extracting the aqueous solution with ether or similar organic solvent; the distribution ratio of most organic bodies is largely in favor of the ether phase, whereas that of inorganic bodies is almost wholly in favor of the aqueous phase, so that repeated extraction with ether will give a nearly perfect separation in the majority of instances. It is frequently possible to increase the ratio in the desired direction by addition of another compound which depresses the dissociation of the substance being extracted; an organic acid of moderate strength for example can be most advantageously extracted from water after addition of a strong inorganic acid, which by its excess of hydrogen ion will convert the organic acid chiefly into undissociated molecules, which are soluble in the ethereal phase whereas the ions are not. An organic base, by the same reasoning, is most easily extracted

in the presence of a strong inorganic base. The addition of neutral bodies such as salts will also in many cases lower the solubility of the organic compound in water (the so-called salting-out effect) and thus favor the extraction by the ether.

In the majority of extraction processes there has been no extended study as to distribution constants, degree of association, dissociation or combination, but the most appropriate extracting agent has been found by the method of trial. There is, however, in all cases, a general principle of great value which can be applied in determining the best method of extraction with a given quantity of extracting liquid, for it can be shown that extraction by means of several fractions of the liquid is more complete than if the whole liquid be used in a single extraction. A simple example will make this point clear. Let a liter of an aqueous solution be considered, holding 100 gms. of an organic compound, and let one liter of ether be considered as the extracting liquid; further, let the distribution ratio of the compound in ether and water be 2. It is apparent that if the whole sample of ether be used in a single extraction of the liquid, the amount dissolving in the ether will be 66.7 gms. If on the other hand the extraction be carried out with two 500 cc. samples consecutively, 50 gms. will be extracted on the first treatment, and 25 gms. on the second, raising the total yield from 66.7 gms. to 75 gms. If now the extraction be conducted with ten 100 cc. samples of ether, the amounts extracted by the successive operations will be 16.67 gms., 13.89 gms., 11.58 gms., 9.65 gms., 8.03 gms., 6.70 gms., 5.58 gms., 4.65 gms., 3.88 gms., 3.23 gms., making a total of 83.86 gms. In the majority of instances, the distribution ratio is far more favorable than the 2 : 1 ratio here assumed, so that extraction approaching 100 per cent can frequently be effected with comparatively few operations. In all cases, however, extraction by fractional parts is more efficient.

If the distribution ratio is known for the materials contained in a given extraction, it is possible to derive a generalized formula which will show the amount still unextracted after a given number of operations.[1] Let W cc. of a solution containing x_0 gms. of a substance be repeatedly extracted with L cc. of a given solvent. After the first extraction, let x_1 represent the number of grams remaining unextracted. The concentration in the extracting phase will then be $\frac{x_0 - x_1}{L}$ and in the original solution $\frac{x_1}{W}$. The distribution ratio K will then be, by definition,

$$\frac{x_1}{W} \div \frac{x_0 - x_1}{L} = K,$$

whence

$$x_1 = KW \times \frac{x_0 - x_1}{L} = x_0 \frac{KW}{KW + L}.$$

[1] Taken from Herz, Der Verteilungssatz, Stuttgart, 1909, p. 5.

After a second extraction x_2 gms. remain in the original solution; the equation takes then the corresponding form

$$x_2 = x_1 \frac{KW}{KW + L}.$$

If now the former value for x_1 be substituted in the equation,

$$x_2 = x_0 \frac{KW}{KW + L} \cdot \frac{KW}{KW + L} = x_0 \left[\frac{KW}{KW + L} \right]^2.$$

Putting the equation now in a generalized form, after the nth extraction, the residual quantity x_n is as follows:

$$x_n = x_0 \left[\frac{KW}{KW + L} \right]^n.$$

Inspection of this generalized formula shows that for the residue x_n to be very small, the distribution constant K should also be small (i.e., the distribution ratio toward the phase being extracted should be small), and the number of extractions, n, should be large.

Temperature Coefficients: A change in the distribution ratio with change in temperature may be anticipated from the fact that the solubility of a substance ordinarily changes with the temperature and that the changes are usually of different magnitude in the two different solvents used. Forbes and Coolidge [1] have derived the temperature coefficient of the distribution ratio of succinic acid in water and ether from solubility data, and obtain a calculated coefficient of 0.0258 per degree, in good agreement with the experimental figure 0.0255. Hantzsch and Sebaldt [2] find that the distribution ratio of acetic acid between water and ether varies only from 2.031 at 0° to 2.19 at 25°, and that of mercuric chloride under the same conditions from 0.391 to 0.429; between water and toluene [3] the distribution ratio of acetone falls from 2.09 at 0° to 1.95 at 30°, and that of mercuric chloride in the same solvents from 12.35 at 0° to 11.25 at 50°. These are all rather small changes, and have led to the loose but useful generalization that temperature changes have but small influence upon distribution ratios. This must frequently be the case, since the distribution ratio alters only with the *difference* between the solubility ratios. In cases, however, where the temperature coefficients of solubility in the two phases are widely different, as where the solubility coefficient is positive in one solvent and negative in the other, large changes in the distribution ratio must result. The same condition will result if any equilibrium is more largely affected by temperature change in the one phase than in the other, whether the reactions be those of dissociation, association, or compound formation. Thus Hantzsch (*loc. cit.*) and his co-workers found that the distribution

[1] *J. Am. Chem. Soc.*, **41**, 150 (1919). See also MacDougall, *ibid.*, **41**, 1718 (1919).

[2] *Z. physik. Chem.*, **30**, 258 (1899).

[3] Hantzsch and Vogt, *Z. physik. Chem.*, **38**, 705 (1901).

of ammonia and amines between water and water-like compounds such as glycerine or ether on the one hand, and hydrocarbons or similar liquids on the other hand, shows a very pronounced temperature coefficient, which they ascribe to the formation of hydrates or similar compounds.

On theoretical grounds it may be assumed that pressure changes also affect distribution ratios between liquid phases, since solubility is affected by the pressure; but such effects must be of exceedingly small magnitude, and have not as yet been noted.

Limitations in Application of the Distribution Law: It has been pointed out that the strict application of the distribution law in gas-liquid systems is limited to dilute systems. The same limitation applies when the phases are two liquids. There is also here the additional limitation that the two liquid phases shall not change their mutual solubility with change of concentration of the distributed phase. Further, corrections in the formula are necessary for each equilibrium affecting the distributed compound in either phase, whether of dissociation, association or chemical combination. In view of these numerous correction factors, which frequently cannot be applied with exactness because of our lack of knowledge of the equilibria concerned, it is not surprising that absolute constancy in the distribution ratio between two liquids has rarely, if ever, been found. It is obvious, therefore, that the distribution principle is interwoven into the problem of the condition of dissolved bodies, concerning which our knowledge is far from complete.[1] Because of this interrelation it is the part of wisdom to accept the distribution law tentatively as valid and make use of it in gaining information as to the nature of the changes which a body undergoes upon being dissolved in a liquid.

Distribution in the System Liquid-Solid

In extending the distribution law to systems containing a solid phase, the only new point of view necessary concerns a solid body as a solvent. A more complete presentation of this topic will follow in the discussion of the phase rule. For the present purpose it is sufficient to look upon a solid solution as a substance as truly homogeneous as a liquid solution, but with the physical attributes of the solid condition instead of the liquid condition. The distribution ratio of a substance between a solid and a liquid phase will be the ratio of its solubilities in the solid and liquid. Solids do not so frequently show solvent properties as do liquids; thus ice is not a solvent for countless compounds which dissolve freely in liquid water; but a certain number of other solids have been found to possess this property, and, in certain of such cases, the distribution law has been tested. Table IX gives the results of Beckmann's [2] experiments on the distribution of thiophene between liquid benzene and solid benzene and Bruni's [3] work on piperidine in the same two solvents.

[1] See Hantzsch and Sebaldt, *loc. cit.;* Hantzsch and Vogt, *loc. cit.;* Georgivics, *Z. physik. Chem.*, **84**, 353 (1913) and **90**, 47 (1915); Smith, *J. Phys. Chem.*, **25**, 160, 204 and 605 (1921).

[2] *Z. physi . Chem.*, **22**, 612 (1897).

[3] *Gazz. chim. ital.*, **28**, 1, 259 (1898).

The columns headed C_l represent the percentage composition of thiophene or piperidine in the liquid benzene and those headed C_S represent their concentration in the solid benzene. The temperatures are the freezing point temperatures of the benzene solutions, slightly lower than the freezing point of pure benzene (5.48°).

TABLE IX

DISTRIBUTION OF THIOPHENE AND OF PIPERIDINE BETWEEN LIQUID BENZENE AND SOLID BENZENE

Thiophene			Piperidine		
C_l	C_S	C_S/C_l	C_l	C_S	C_S/C_l
1.22	0.48	0.396	0.553	0.072	0.13
2.28	0.99	0.434	1.37	0.155	0.11
2.87	1.29	0.459	2.57	0.216	0.09
3.42	1.49	0.437	3.21	0.313	0.10
4.50	1.87	0.414	4.20	0.499	0.12
6.44	2.66	0.413	4.68	0.615	0.13
11.20	4.38	0.391			
16.60	6.29	0.379			

From the constancy of the ratios C_S/C_l, it is apparent that both thiophene and piperidine possess the same molecular condition in solid benzene as in its liquid form. It will also be noted that the solubility of thiophene in solid benzene is very considerable, amounting to about 4/10 of its solubility in the liquid; it is evident therefore that purification of benzene from thiophene by the method of crystallization is beset with difficulties. Iodine has also been found [1] to have a relatively high solubility in solid benzene and to possess normal molecular weight in both the liquid and solid solvent.

In the above examples, the same substance figures as solvent in both the solid phase and the liquid phase; the distribution follows the same principle, however, when the solid phase is of different composition. As an example, there are given in Table X figures on the distribution of thallous nitrate between solid potassium nitrate and an aqueous solution, as determined by Fock.[2] It

TABLE X

DISTRIBUTION OF THALLOUS NITRATE BETWEEN SOLID POTASSIUM NITRATE AND AQUEOUS SOLUTION

Conc. KNO_3	C_l	C_S	C_l/C_S
3.2658	0.3238	2.77	0.117
3.2944	0.1869	1.78	0.105
3.2981	0.0663	0.57	0.116
3.2851	0.0231	0.20	0.116
3.2515	0.0089	0.08	0.111

[1] van't Hoff's Lectures, II, 75.

[2] *Z. Krystall.*, 28, 337; *Zentral.*, 1891, I, 710; taken from Lewis, Physical Chemistry 1916, p. 344.

is of course necessary that the solution be saturated with the potassium nitrate in order that the solid phase may be present.

The concentration of this salt, expressed in moles per liter of aqueous solution is given in the first column. The concentration of the thallous nirate in the liquid phase (C_l) is given in column 2 and its concentration in the solid potassium nitrate in column 3 (C_S), both expressed in moles per 100 moles of solution; the ratio C_l/C_S given in column 4 is satisfactorily constant, and again shows that the molecular condition of the thallous nitrate is the same in both solvents. Ionization has been reduced to a minimum in the aqueous phase by the common ion from the large excess of potassium nitrate.

Distribution in Other Systems

Where two phases are under discussion, the possibilities as to combinations in which distribution might occur are the following: gas-liquid, liquid-liquid, liquid-solid, gas-solid, solid-solid. Two gaseous phases are impossible, since all gases are completely soluble. Three of these five combinations have been discussed above; the discussion of the remaining two may be made brief. Distribution between a gaseous phase and a solid phase of course requires that the distributed compound be itself a gas, and capable of dissolving in the solid. That such cases occur is in accord with the well-known diffusion of hydrogen through platinum or palladium, but the solubilities are usually of a low order; when large apparent solubilities are found, the result is frequently to be attributed to adsorption upon the surface of the solid, and results are obtained which are not easily interpreted in terms of the distribution law. A number of interesting cases have been investigated by Sieverts and his co-workers,[1] by whom the solution of several gases in common metals was quantitatively examined. The figures for the solubility of hydrogen in nickel are given below.

TABLE XI

Solubility of Hydrogen in 26.97 Gms. Nickel

1st Series: Temp. = 923°			2d Series: Temp. = 822°		
Pressure in Cm. of Hg	Cc. of H_2 Dissolved	$\frac{\sqrt{p}}{m}$	Pressure in Cm. of Hg	Cc. of H_2 Dissolved	$\frac{\sqrt{p}}{m}$
764	2.63	10.5	764	2.20	12.6
663	2.50	10.3	660	2.08	12.4
584	2.39	10.1	583	1.93	12.5
448	2.06	10.3	529	1.86	12.4
319	1.62	11.0	447	1.71	12.4
164	1.11	11.5	318	1.41	12.7
129	0.98	11.6	165	1.01	12.7
			132	0.89	12.9
			88	0.72	13.0
			52	0.50	14.4

[1] *Z. physik. Chem.*, **60**, 129 (1907), **68**, 115 (1910); *Ber.*, **42**, 338 (1909), **43**, 893 (1910), **45**, 221 and 2576 (1912).

In these experiments, as in most others in which a gas is dissolved by a solid, it appears that the solubility is not directly proportional to the pressure, as would be the case if Henry's law expressed the conditions, but is proportional to the square root of the pressure; as interpreted previously, this indicates that the gases in the solid solution have one half the molecular weight which they possess in the gaseous condition, that is, that hydrogen and other elementary gases are present in monatomic condition in the solid phase. An equally simple interpretation for the case of sulphur dioxide in molten copper is not available. The difficulty was elucidated by Stubbs[1] who showed that interaction with the copper occurs.

The solubility or insolubility of a given gas in a given metal has naturally a very important bearing upon the use of the metal as a catalyst in reactions in which the gas takes part; Sieverts gives the following classification of cases studied by him:

nitrogen: not dissolved by metals except by iron and aluminium with the formation of nitrides.
carbon dioxide: insoluble in copper.
carbon monoxide: soluble in nickel; insoluble in copper.
oxygen: soluble in (molten) silver.
sulfur dioxide: soluble in (molten) copper.
hydrogen: soluble in copper, nickel, iron, palladium; insoluble in cadmium, thallium, zinc, lead, bismuth, tin, antimony, silver and gold.

It will be shown, however, in Chapter XV that it is the adsorbed gas rather than the dissolved gas which is really important in catalytic work.

For solid-solid systems the available data are meager; although two solids may frequently show mutual solubility, which will be discussed under the phase rule, the equilibria are usually attained only after long intervals, and independent analyses of the phases are not easily made. For these reasons application of the distribution law has rarely been attempted.

When three-phase systems are considered, the distribution law is still applicable. The simplest application would be when the gaseous phase over two liquid phases is taken into the calculation. It is apparent however that with increase in the number of phases the possibilities as to association, dissociation and chemical combination are likewise increased, and the application of the distribution law becomes increasingly difficult.

THE PHASE RULE

The most useful generalization relating to the physical and chemical reactions which occur in heterogeneous systems is the phase rule of Willard Gibbs.[2] Published in a journal not widely read and developed in a mathematical fashion, its fundamental value was not at once recognized. It is owing to the subsequent adoption of the phase rule by Roozeboom, Ostwald and van't Hoff that it has become generally known to chemists and physicists as a principle of the widest applicability, of the highest value in the classification of heterogeneous equilibria and of the greatest reliability in the settlement of disputed points; van't Hoff made use of the rule in many of his published investigations, Roozeboom made it the basis of his monumental monograph,[3] Die heterogenen

[1] *J. Chem. Soc.*, **103**, 1445 (1913); *Proc. Chem. Soc.*, **29**, 225.

[2] Gibbs, *Transactions Connecticut Acad.*, 1874–1878; also in Gibbs' Collected Scientific Papers, Longmans, Green and Co., 1906; The Collected Works of J. Willard Gibbs, Ph.D., LL.D., Longmans, Green and Co., N. Y., 1926.

[3] Roozeboom, Die heterogenen Gleichgewichte, Braunschweig, 1901 et seq.

Gleichgewichte, and Ostwald adopted it as his basis of classification in his Lehrbuch.[1] Roozeboom had previously been making use of the phase rule in his investigations beginning as early as 1884 to 1887,[2] at the suggestion of van der Waals. It has since this time come into very general use, and has the advantage over others of our commonly accepted generalizations in that it contains no assumptions based upon theory, such as the molecular hypothesis, the kinetic theory, theories of constitution of matter or of chemical reaction, and is therefore not subject to revision or rejection as our views of these matters may change.

In order to appreciate the importance of Gibbs' generalization, it is necessary to have an idea of the type of phenomena with which the phase rule is concerned. In a general way it may be stated that the effect of changing temperature, pressure or concentrations in any heterogeneous system would have to be considered a special problem for each system investigated were it not for the phase rule; by its means, however, the effect of these changing conditions can be shown to follow a definite rule for all systems. A few instances will illustrate the point. Three open flasks may be taken, containing respectively pure water, a dilute solution of hydrochloric acid and a dilute solution of sodium chloride; if these three liquids be heated, their behavior will be entirely different. The water will undergo a steady rise of temperature until its boiling point of 100° is reached, at which point the liquid will boil away without change of temperature until the flask is dry. In the second case, the liquid will begin to boil at some temperature not far from 100° but the temperature will still continue to rise and the solution become more and more concentrated with respect to hydrochloric acid until a temperature of 110° is reached, at which point the liquid will continue to boil without change of temperature or of composition until this flask also is dry. In the third case the liquid will also begin to boil at a little above 100°, and again the temperature will rise until, at about 107°, solid sodium chloride begins to precipitate; the temperature will then remain constant while the remainder of the water boils off, leaving the dry salt behind. The widely different behavior of these three solutions has of course long been known; but it remained for the phase rule to show that the three cases could all be interpreted in terms of a single law. In like fashion, if the three solutions were subjected to conditions which would withdraw heat from them, the first would show a constant temperature only once during the withdrawal, the third twice and the second a number of times—explicable again in terms of the same phase rule. In short, a very large number of previously unrelated phenomena, dealing with changes involving several phases, have been clearly and intelligibly related by means of the phase rule, and predictions as to countless reactions not yet investigated may be made with complete safety.

The Phase Rule: The phase rule of Gibbs is stated in terms of the number of phases present in a system at equilibrium, the number of components from

[1] Ostwald, Lehrbuch der Allgemeinen Chemie, 2d Edition, Leipzig, 1903.

[2] Die heterogenen Gleichgewichte, I, p. 7.

which the system can be built up, and the number of conditions (pressure, composition or temperature) which may be varied without causing a change in the number of phases. In words the statement of the relationship is somewhat cumbersome, but it may be very simply expressed by the equation

$$F = C - P + 2,$$

in which C stands for the number of components of the system, P the number of phases present, and F the degree of freedom, or the variance, of the system. Before passing to the application of this rule to any system under observation, it is necessary that each of the terms used, either in a verbal statement of the rule or in the equation, should be accurately defined and thoroughly understood. The list includes the terms equilibrium, phase, component, and degree of freedom.

Equilibrium: An equilibrium exists in any system under a fixed set of conditions when the parts of the system do not undergo any change of properties with the passage of time, provided (which is the crux of the statement) that the parts of the system have these same properties when the same conditions are again arrived at by a different procedure. It is this provision which makes possible the distinction between stable equilibrium and metastable equilibrium; in both cases the system may be capable of maintaining itself perhaps indefinitely without change, but in the case of metastable equilibrium an alteration in the method of producing the system will give us an entirely new set of properties. As an example of this distinction, let a vessel of water be considered which is cooled slowly and carefully to a temperature of $-1°$; with care such a system may be maintained as long as desired, and will consist of water of a certain density and vapor of a certain pressure. It appears then that the system is in equilibrium. Again, ice at some low temperature may be carefully warmed to $-1°$, when it will have a fixed density and a fixed vapor pressure somewhat lower than that of the former system; equilibrium appears to exist in the second case also. The distinction lies in the fact that this second system may also be produced by cooling water, while the first can never be produced by warming ice; ice and vapor at $-1°$ may then be considered a system in stable equilibrium, while water and vapor at $-1°$ are in metastable equilibrium.

In making use of the phase rule, it is a matter of the most fundamental importance to remember that it applies to systems in true equilibrium and only when they are in true equilibrium. If the mathematical application of the rule shows, in some of the cases to be studied, that only a certain number and class of phases can be present at equilibrium, the conclusion of course is not justified that no other number of phases can be present; if the system is not in temperature equilibrium (i.e., if different parts of it have different temperatures) or if the phases are out of equilibrium (i.e., the phase reactions have not been completed), the system may be quite different from that which would be deduced by the phase rule. Practical experience with conventional ice water will convince anyone that it is possible to have ice, water and vapor in a tumbler

many degrees above zero, and the experience does not constitute a contradiction of the phase rule; it indicates only that we frequently drink the liquid before equilibrium has been attained. Nor does the phase rule give any indication of the rapidity or slowness with which a given equilibrium is reached or how it is most easily produced; it is severely limited to an exact statement of the existing conditions when equilibrium has been attained, in the sense in which equilibrium has been defined above.

Phases: The term phase has for some time been a part of the nomenclature of elementary chemistry; the concept is simple and easily grasped. A phase is any part of a system, which is homogeneous throughout; it is bounded by a surface and is mechanically separable from the other parts of the system. Such a phase is necessarily in one of the three physical states of aggregation, gaseous, liquid or solid. Since all gases are found to be mutually soluble, that is, to pass into a homogeneous condition, it follows that there can be only a single gaseous phase in any system under consideration; with liquids complete solubility is by no means always the case, and there may therefore be several liquid phases present in certain systems, and the same is true for solids. However many liquids or solids may have been formed under varying conditions from the components of a given system, in no case has the number of liquid phases coexisting at equilibrium been found greater than the number of the components in the system, and the number of coexistent solid phases at equilibrium cannot exceed the number of components by more than two, as will be shown later. With regard to the composition of the gaseous, liquid and solid phases, the phase rule makes no assumption as to their classification as elements, compounds or solutions, and distinguishes only between phases of fixed composition and those of variable composition; but, if the customary chemical method of classification be used, it may be stated that any phase, whether gaseous, liquid or solid, may be composed of an element, a compound, or a solution of elements or compounds, since all these forms are homogeneous. Mixtures only are excluded, since, by definition, a mixture is heterogeneous and therefore composed of at least two phases. Finally it should be pointed out that a phase need not be continuous; the gaseous phase, because of the diffusibility of gases, is generally continuous in any system, and the liquid phase because of the fluidity of liquids is usually so, though it may of course be broken into droplets by agitation; solids however are commonly present as discontinuous fragments. Continuity is excluded from the definition of a phase, since discontinuity brings about no change except one of surface, which will be discussed in the paragraph on variables. Gibbs[1] in introducing the term phase states that it refers "solely to the composition and thermodynamic state of any body without regard to its quantity or form."

Components: The concept of the components is frequently less easily grasped than the other necessary concepts by those taking up, for the first time, the study of the phase rule. This is, perhaps, because of a double use to which we put the term. It is necessary to derive, in the first place, the

[1] Scientific Papers, p. 96.

number of components, in order to have a numerical value to substitute for the term C in the phase-rule equation; it is also frequently useful to name the *individual components* in terms of which the composition of the various phases is to be expressed. The number of components must have a perfectly definite value, derivable in a systematic manner, and subject to no arbitrary desire on the part of the investigator. The individual components on the other hand, while limited in number as stated, may be chosen at will within certain limits, as will be shown; there is here a certain freedom of choice not permissible in the former instance.

The *number of components* of a system at equilibrium is defined as the smallest number of independently variable constituents by means of which the composition of each phase may be mathematically expressed. In accordance with this definition it is possible, though it is not the usual practice, to determine this number without any reference to what the individual components may be. This may be done, for example, by determining the value of C in the equation when the other variables (F and P) are known. It is also possible to arrive at the number empirically, from analysis of all the phases present; if they are all of the same composition (under varying conditions), the system is of one component, if the phases present can be produced from any two phases, the system is of two components, while if more phases are necessary to express the composition of any one, the number of components is represented by that number of phases. More commonly, however, the number of components is deduced from knowledge as to the physical or chemical changes which the system undergoes. Thus if the decomposition of calcium carbonate by heat is being studied, it is known that the phases present consist of a gaseous phase composed chiefly of CO_2 with whatever traces of $CaCO_3$ and CaO are capable of volatilization, and two solid phases, CaO and $CaCO_3$. It is clear that from two components, most simply CO_2 and CaO, the composition of each of these three phases may be expressed in the usual terms of percentage by weight, or in terms of other units; a smaller number (one) is incapable of doing this. In expressing the composition of the solid CaO, the amount of CO_2 is zero; neither zero values nor negative values however are excluded by the definition given. If we now consider what *individual components* shall be chosen in discussing this system, it would be wisest to choose CO_2 and CaO, since minus quantities will then not enter into any statement of composition and graphical representation will be most simple; but other choice may be made, since the composition of any phase can be expressed in terms of any two of the components, by use of zero or negative coefficients. It happens that, in this instance, each phase is of constant composition, but in some two component systems the composition of some phase, namely, a solution, may vary from 0 per cent of component A and 100 per cent of component B to 100 per cent of A and 0 per cent of B.

The number of components of a system may differ also with the conditions under which its equilibria are being studied. Thus, water is commonly regarded as a one-component system because, under the ordinary conditions of

experimentation, the three phases found (ice, liquid and vapor) may all be expressed as composed of water alone; but if temperatures are raised until the dissociation of water has begun, according to the equilibrium

$$2H_2 + O_2 \rightleftharpoons 2H_2O,$$

it would no longer be possible to express all possible compositions in terms of water; for, if excess hydrogen or oxygen be introduced, the composition of the vapor phase can be expressed only in terms of two components, hydrogen and oxygen, whose concentrations can be independently varied. *The number of components* then, while always definite, may vary with the condition of the system, and is arrived at in accordance with the definition given; the *individual components* may be chosen according to convenience from among the substances taking part in the equilibrium.

It is upon the basis of the number of components that systems are classified for phase-rule study as one-component systems, two-component systems, etc.

Degree of Freedom (Variance of a System): In the application of the phase rule, the independently variable conditions which are taken into consideration are three in number—*temperature*, *pressure*, and *composition*. This restriction of the types of independent variables to three is of course arbitrary; usually the effects of gravitation, of electrical condition, of surface energy and of light absorption are purposely excluded. It is necessarily true that these variables may have an effect upon the equilibrium existing between various phases, but in large numbers of cases their effect is negligibly small; in the cases where their effect is large, the phase rule as here given affords but small help, as in the field of colloid chemistry, where surface energy is the most influential factor. If only these three variables are considered, it follows that when these three are known the system may be regarded as defined; that is, a complete statement of the properties of each phase is implied by the statement of the three variables. Thus, to state that a gaseous system contains 50 per cent each of carbon dioxide and nitrogen at 20° C. and 760 mm. pressure of mercury, defines the system in that any other sample of these gases made up according to the same conditions will be identical with the first in all properties except mass.

It is however not necessary in all cases to fix as many as three conditions in order to define the system under observation, and it is precisely the number of these variables which must be arbitrarily fixed, in order completely to define the system, that is called the *degree of freedom* of that system. The mixture of gases mentioned above is obviously a system with three degrees of freedom, since a statement of a temperature, a pressure and a concentration were necessary; if the system to be defined is a saturated solution of sodium chloride with excess solid and vapor, we need mention only the desired temperature (one degree of freedom), while for a system of ice, water and vapor no further statement of condition is necessary. The specific application of this principle will appear in the examples to be studied; it will suffice for the present to state the customary nomenclature, which is to describe systems with no degree of

freedom as *invariant*, those with one degree of freedom as *univariant*, those with two as *bivariant*, and so on for other multivariant systems. The possibility for a system to have a variance greater than three, where only temperature, pressure and composition are the variables, lies in the fact that, for multicomponent systems, knowledge of the concentration of more than one component is necessary in order to state the composition; thus, in a solution containing three components, the composition with respect to two must be stated before the composition of the solution is known.

Further Restrictions: In the application of the phase rule equation, it frequently happens that there are certain additional restrictions which must be taken into account in the equation. The mathematical effect of any such additional restriction is to decrease by one the value of the terms upon the right hand of the equation $F = C - P + 2$, which means necessarily to reduce the number of degrees of freedom by one. This would be the same in effect as increasing the number of phases by one, and is usually viewed in that manner. An illustration will make the practice clear. If the substance under investigation were ammonium chloride, which decomposes according to the equation

$$NH_4Cl \rightleftharpoons NH_3 + HCl,$$

it is clear that the system is a two-component system since, if all possible relationships in the gaseous phase are studied, varying amounts of NH_3 and HCl must be added, and the composition of the gaseous phase cannot be expressed by fewer components than those two. But, let the restriction now be imposed that the NH_3 and HCl shall always be in the molecular ratio 1 : 1; i.e., that no excess NH_3 or HCl shall be added; the system may under these conditions be treated literally as a one-component system since the composition of either phase may be regarded as NH_4Cl, and it will have the number of degrees of freedom corresponding to a one-component system. Again, in the study of a liquid which undergoes the critical phenomena at its critical temperature, it might appear, since we have only two phases present, that the system is univariant, since substitution of 1 for C and 2 for P gives $F = 1$; actually however the statement that the substance is undergoing the critical phenomena imposes an additional restriction included in the definition of the critical state, which is that the two phases shall be identical. This restriction reduces the degrees of freedom by one and indicates that the system is invariant, which means that the critical phenomena occur only at a fixed and unvarying temperature and pressure for a given liquid. This is of course in accord with the facts; the omission of the added restriction would lead to the entirely false conclusion that the system is univariant and that the experimenter might therefore determine for himself at what temperature or at what pressure the liquid might be made to pass into the critical condition. Indeed, it is just this restriction which differentiates a one-component liquid at its boiling point, which is a state of univariant equilibrium and the temperature of which can be altered by changing the pressure, from the same liquid at its critical temperature, when the system is invariant.

Derivation of the Phase Rule: With the various terms of the phase rule discussed, a brief statement of its method of derivation may be made. The rigorous thermodynamic derivation which Gibbs made is abstract and difficult; the reader is referred to Gibbs' papers (*loc. cit.*) for details, or to other extended treatises.[1] The following is not given as a rigorous derivation, but is nevertheless useful in showing in a general way the method of derivation which Gibbs used.

It has previously been shown that the degree of freedom (F) of a system is the number of variables which must be arbitrarily fixed in order to define the system. It follows simply enough that the number of such variables must be equal to the total number of variables of the system minus the number of variables which are defined by the system itself; that is,

$$F = \text{(total variables of the system)} - \text{(defined variables)}.$$

A numerical statement of these two terms in the equation, if it can be put in such fashion as to include only the number of phases and number of components, will give the phase rule equation.

The total number of variables can easily be calculated. As stated above, they may be the variables of temperature, of pressure and of composition. There can be but one temperature and one pressure throughout a system at equilibrium, so that the temperature and pressure variables total two. The composition variables however may be numerous. In each phase the composition may vary, and within each phase the number of variations in composition is equal to the number of components less one, i.e., to $(C - 1)$, since for two components we may vary the percentage composition with respect to one of them and derive the second by difference, and for three components by similar reasoning we may vary two. The total number of composition variables in all the phases is therefore $P(C - 1)$, and the total number of variables of all kinds is greater by the two variables of temperature and pressure, so that the total number of variables to be set in the equation above is $P(C - 1) + 2$.

In order to calculate the second term, the number of variables defined by the system itself, Gibbs introduced the concept of the thermodynamic or chemical potential which each component possesses, and which is the intensity factor of the chemical energy of that component. In a system at equilibrium this chemical potential of each component must be the same in each phase, just as for thermal equilibrium the temperature, which is an intensity factor, must be the same in all parts. The potential of a given component in a given phase is a function of the temperature, the pressure and the composition of that phase and an equation exists relating the potential to those three variables.[2]

[1] Roozeboom, Die heterogenen Gleichgewichte, I, 21; Partington, Thermodynamics. D. van Nostrand, 1924.

[2] It is worth noting that the actual *mass* of the phase plays no part in the equation, and hence has no influence upon the equilibrium. This is a fundamental feature of heterogeneous equilibria. It was recognized before the statement of the phase rule, and finds expression for example in the well-known tenet that in mass-law equilibria the " active mass " of the solid is constant.

Another equation exists for this same component in each other phase, giving a number of equations equal to P; but since the potential is the same in each case, it follows mathematically there will be only $P - 1$ independent equations for that component. The fact that these equations may have a form and value unknown to us is of no importance; the essential is that there are $P - 1$ relationships which actually define the potential of that component in the system. Since what is true for one component is true for all, there are $C(P - 1)$ relationships existing in the system which define the chemical potential of all the components, and hence define the equilibrium.

It remains only to insert these two terms in the equation given above:

$$F = [P(C - 1) + 2] - [C(P - 1)] = C - P + 2.$$

Systems of One Component

When a system consisting of a single component is considered, it follows, by substitution in the phase-rule equation, that it is bivariant if it exists in but one phase, univariant if it exists in two phases, and invariant if it exists in three. Since the number of phases cannot be less than one, the degree of freedom of such a system cannot exceed bivariance. The independent variables are limited to the pressure and the temperature, since all phases are alike in composition.[1] If it is assumed that such a system can have but one vapor phase, one liquid phase, and one solid phase, the following classification of systems may be made, in which the symbols V, L, and S stand respectively for vapor phase, liquid phase and solid phase:

Bivariant	Univariant	Invariant
V	$L + V$	$S + L + V$
L	$S + V$	
S	$L + S$	

More than a single vapor phase cannot be present, since gases or vapors are always mutually soluble, and more than a single liquid phase is also unknown, though it is possible to regard liquid crystals as constituting a second liquid; of solid modifications (polymorphic forms) there may be a large number. If a second such solid form exists, the number of possible equilibria is increased by seven, since it can exist alone or in contact with each of the other three forms or in contact with each of the three combinations of two forms; the existence of a third solid form will of course increase the number of possible systems still more largely. It does not follow however that all of these systems which may be conceived as algebraical possibilities shall be capable of experimental realization; sometimes such equilibria can be shown to be necessarily impossible,

[1] This statement is true only in a restricted sense. The amount of material per unit volume, or density, of course varies from phase to phase, and the density (or specific volume) may therefore be regarded as a third independent variable. The familiar diagram of the pressure-volume relations of the gaseous and liquid state, showing the equality of volumes at the critical point, is the commonest example in which the volume is treated as an independent variable.

and in many other cases the experimental requirements of temperature or pressure cannot be met. Nevertheless, the number of such typical systems which have been studied is very large, indeed much too large for systematic treatment within the limits of this chapter; still less will it be possible to illustrate all possible types of equilibria for two-component or multi-component systems. A few examples of the better known one-component, two-component and three-component systems will be discussed, with whatever generalizations may be drawn from them; for more exhaustive study, the student is referred to any of the several treatises on the phase rule.[1]

Water: In proceeding to a study of this substance, it will be simplest if we recount the well-known facts with reference to its occurrence in different phases and then interpret them in terms of the phase rule. These outstanding facts are that the liquid has a vapor pressure which increases with the temperature (amounting to 760 mm. of mercury at 100°, which is its boiling point) until the temperature reaches 374° C., at which point it undergoes the critical changes; that, upon cooling, it freezes to form ice at 0° under atmospheric pressure, which solid also has a small but measurable vapor pressure; and, lastly, that this freezing point is lowered by increased pressure. The statement of these well-known facts implies the following phase equilibria: (1) liquid water and its vapor, in which the vapor pressure increases with the temperature, (2) ice and vapor, in which the vapor pressure and temperature bear a similar relationship, (3) solid and liquid, in which the melting point decreases with pressure increase, and (4) solid, liquid and vapor, existing together only at a fixed temperature of approximately 0° C. In these four equilibria, pressure and temperature are the only variables mentioned; in this system there can be no variations in composition, since each phase is wholly water under all conditions. The quantitative data for these relationships are given in the following table.

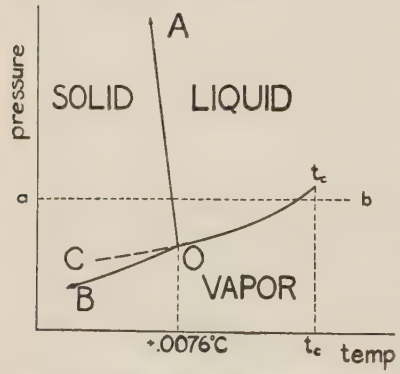


FIG. 4. *p.-t.* Diagram for Water (Schematic)

The same data are shown schematically in Fig. 4, in which the pressure is written as ordinate and the temperature as abscissa. Three curves result, representing the three univariant equilibria. The curve COt_c, which will be discussed first, represents the equilibrium between liquid water and vapor, and is the so-called *vapor pressure curve for water*. For every temperature there

[1] Die heterogenen Gleichgewichte, Braunschweig; vol. 1 and 2, I by Roozeboom, 1901 and 1904; 2, II by Buchner, 1918; 2, III by Aten, 1918; 3, I and II by Schreinemakers, 1911 and 1913. The Phase Rule, by Bancroft, 1897. The Phase Rule and its Applications, Findlay, 1927 (6th edition). The Principles of the Phase Theory, Clibbens, 1920. Gesättigte Salzlosüngen vom Standpunkte der Phasenlehre, Jännecke, 1908. The Phase Rule, Rivett, 1923. Equilibrium in Saturated Salt Solutions, Blasdale, 1927.

TABLE XII

EQUILIBRIUM PRESSURES FOR WATER

Temp. C.	Water + Vapor $L \rightleftharpoons V$	Ice + Vapor $S \rightleftharpoons V$	Ice + Water $S \rightleftharpoons L$
− 20		0.770 mm. of Hg	1970 kg. per sq. cm.
− 15		1.237 " " "	1590 " " " "
− 10	2.144 mm. of Hg	1.947 " " "	1130 " " " "
− 5			610 " " " "
0	4.579 " " "	4.579 " " "	1 atmosphere
+ 20	17.539 " " "		
+ 100	760.00 " " "		
+ 200	15.3 atmospheres		
+ 300	84.6 "		
+ 374	217.5 "		

exists one pressure, and only one, which can be exerted by the system, and for each pressure one temperature and only one at which equilibrium can be maintained, which is simply the more lengthy way of stating that the system consisting of liquid water and vapor is univariant, and that the selection of a temperature defines the pressure or the selection of a pressure defines the temperature. This will be recognized, also, as a restatement of the long-known fact that the vapor pressure of water depends only upon the temperature. If, however, at a given temperature, a pressure is maintained above that indicated on the line Ot_c, the vapor will be compressed wholly into the liquid phase; or if the pressure is maintained below the equilibrium pressure, the liquid will wholly evaporate.

Our information about the vapor tension curve COt_c might be called complete if we were in position to state its origin, its terminus, and its position at all intermediate points. In the case of water, we have a large part of this information. Careful experimental measurements of the vapor pressure have been made by a large number of investigators, and may be found in the tables of physical constants. Were we not in possession of this material, however, we could at least determine qualitatively that the curve rises with the temperature by the application of the van't Hoff law of mobile equilibrium, which, with Le Chatelier's theorem, is the handiest tool in the application of the phase rule. The change of liquid into vapor is an endothermic change, and hence by application of the rule, the equilibrium will be moved in that direction by a rise in temperature. Further, the Clapeyron-Clausius thermodynamic equation

$$\frac{dp}{T} = \frac{\lambda}{T\Delta V},$$

in which λ is the heat of vaporization and ΔV the change of volume on vaporization, gives the slope of the curve.

The upper end of the vapor-pressure curve for water, or indeed for any liquid, is the critical point t_c, which has been discussed in an earlier chapter. Study of the two phases, water and vapor, shows that, as the temperature and pressure rise, the liquid becomes less dense and the vapor more dense, and the heat of vaporization becomes less and less; if the temperature rise be carried far enough, the two phases will become of the same density and the heat of the change will become zero; or, in other words, the two phases will become identical upon reaching this critical state. In general terms, the critical state is that state, approaching which coexistent phases approach identity, and at which they become identical. For water, the critical temperature is 374° and the critical pressure 217.5 atmospheres; it is an invariant point, since neither pressure nor temperature may be altered. As previously explained, the additional restriction that the two phases shall be identical puts the occurrence in accordance with the phase-rule equation. Above this temperature and pressure, water exists a state for which no general name has as yet been adopted; the distinction between the liquid state and the gaseous state has vanished, and the areas V and L in Fig. 4 pass into each other without discontinuity.

Passing to the lower section of the vaporization curve COt_c, the point O represents the temperature at which water ordinarily freezes. With sufficient care however water may be cooled considerably below this temperature without the formation of ice, and from such experiments a prolongation OC of the vapor pressure curve has been drawn to represent the still perfectly definite relations of pressure to temperature. The extent of this prolongation is, however, indeterminate; the point C therefore represents no definite end to the curve. Throughout the whole course of the section OC the system water + vapor is metastable, in that it will, on contact with a nucleus of ice or sometimes without such contact, change into the system ice + vapor; the irreversibility of this change will appear a little later.

The curve OB in Fig. 4 represents the equilibrium curve for ice plus vapor, and is spoken of as the vapor pressure curve of ice or sometimes as its sublimation curve. Its lower end B is assumed to be at the absolute zero of temperature and the application of van't Hoff's law would again indicate pressure increase with increase of temperature. The experimental figures for this curve, some of which are given in column 3 of Table XII, place the curve below that for water + vapor (OC) throughout its course, but its steeper curvature brings about an intersection of the two at a temperature very close to 0°. The positions of the two curves OB and OC may be used to explain the stability relationships of the two systems. If, at some constant temperature below that of the point O, ice is set in one vessel and water in a second under a bell-jar, the vapor pressure of the system water + vapor will be greater than that of the other, and as a result vapor passing from the liquid will solidify upon the ice until the liquid has entirely disappeared. In such a case it is obvious that the unstable system is the system with the higher vapor pressure.

The intersection of the two curves at the point O represents a new equilibrium. Ice and vapor are in equilibrium, water and vapor are in equilibrium,

and the vapor is the same in pressure in both cases; it follows then that ice and water must also be in equilibrium, and the curve representing that equilibrium (*OA*) must pass through the point *O*, which is therefore the intersection of three curves. Roozeboom first suggested that such a point be called a "triple point." It represents an invariant condition, in which neither pressure nor temperature can be changed without the elimination of a phase. The temperature and pressure corresponding to this triple point have been carefully determined; the pressure is 4.579 mm. of mercury and the temperature + 0.0075°. (The occasion of this variation from the commonly accepted freezing point of 0° will be explained a little later.) At this temperature and pressure, and only here, can a system consisting of water be maintained in the three coexisting states of ice, liquid and vapor.

The triple point *O* has been shown to be the origin of the curve *OA*, representing the equilibrium between ice and liquid in the absence of vapor. It has long been known [1] that the melting point of ice, that is, the equilibrium temperature, is altered by pressure. Whether an increase of pressure will raise or lower the melting point may be easily deduced from Le Chatelier's theorem; increased pressure will shift the equilibrium in the direction which reduces the pressure within the system, which is in the direction producing smaller volume, and since, in the case of water, the liquid has a smaller volume than the solid (i.e., is denser), increased pressure at constant temperature results in liquefying ice. The curve *OA* is therefore inclined upward toward the pressure axis, so that at any temperature represented upon it an increased pressure (measured upward) brings the system into the region of liquid alone; or, otherwise stated, the freezing point is lowered by increased pressure. The curve is not a straight line, but is slightly concave toward the pressure axis; a few of the corresponding pressures and melting points are given in Table XII, column 4.

Before considering the extension of the curve *OA* toward very high pressures, it will be well to compare Fig. 4 with our common knowledge of the behavior of water, upon which we have built our discussion. In one particular, the figure differs from our usual laboratory experience; in laboratory practice the freezing point of water is taken as exactly 0°, whereas in our discussion we have stated it to be + 0.0075°. Line 5 of Table XII shows for 0° a lack of agreement in the pressures of the three monovariant equilibria. We have here, however, no contradictions to the phase rule to explain, nor even inexact data to excuse; the explanation is that our data and our discussion are applicable to systems consisting of water alone, in which the pressure is that caused by water vapor, while our laboratory practice is carried out in open vessels in which a second component is present, namely, air, and in which a constant pressure of one atmosphere is exerted. Since a second component is present, a system consisting of ice, water, and the gas phase is *not* invariant, as may be seen by substitution in the phase-rule equation, but is univariant. and there can be any number of temperatures at which the system can exist with corresponding

[1] James and William Thomson, *Trans. Roy. Soc. Edin.*, 16, 575 (1849); *Proc. Roy. Soc. Edin.*, 2, 267 (1850).

pressures. Actually, however, the effect of the air as an added component is not great, since it is probably not present at all in the solid phase and its solubility in the liquid is not large. More important, however, is the fact that its presence puts the system under a pressure of one atmosphere instead of the small vapor pressure of water, and in accordance with the reasoning already used the melting point of the ice is depressed from + 0.0075° to 0°. The vapor pressures are of course also affected slightly by the change in temperature and composition, but the difference is very small. To state the facts as succinctly as possible, + 0.0075° is the triple point for the one-component invariant system, ice, water and vapor, and the corresponding vapor pressure is 4.579 mm.; 0° is the equilibrium temperature in the two-component system consisting of water and air, where the phases are ice, aqueous solution of air and vapor phase and the total pressure is one atmosphere.[1]

The freezing point of water is one of our best known fixed points and is a standard temperature used in the marking of thermometers. While not independent of the pressure, it varies so slightly that fluctuations of barometric pressure such as occur with changes of weather are negligibly small. Any triple point in a one-component system, or more commonly any one-component solid-liquid-vapor complex in the presence of air at 1 atmosphere pressure, is in principle suitable for the standardization of thermometers; in practice certain invariant systems of two components (air not being considered) are found more convenient, consisting of a salt and water and giving rise to very accurately determined eutectics and transition points of a hydrate to a lower hydrate or to the anydrous form; examples will be given later.

Returning to the fusion curve *OA*, it has been found that at high pressures there exist several polymorphic forms of ice, differing from the common variety in density, heat of formation, crystalline structure and other physical properties. Tammann[2] was the first to discover that, at sufficiently high pressures, new modifications of ice appear, and his work together with that of Bridgman[3] gives a fairly complete picture of the phase relations which exist. There are at least five polymorphic forms of ice, known as ice I (the common form), ice II, ice III, ice V, and ice VI, the positions of which in the $p-t$ diagram are shown in Fig. 5. The relationships of ice IV are not clearly known, and it is not included in the sketch. Each of these five forms has definite limitations of pressure and temperature within which it can exist as a stable form, at the boundaries of which it can exist in stable equilibrium with other forms and outside of which it can have only metastable existence. These boundary curves represent univariant equilibria, in the same sense as the curves studied

[1] More strictly speaking, water and air make up a multi-component system, since the air does not dissolve as such in the liquid, but gives to the water concentrations of oxygen, nitrogen, argon, carbon dioxide, etc., depending upon their solubility and their partial pressure. Since the principal effect of the air is due to its pressure rather than to the components which it adds, this further complexity may be neglected.

[2] *Ann. Physik.*, (4) **2**, 1 and 424 (1900); *Z. physik. Chem.*, **72**, 609 (1910); **84**, 257 (1913); **88**, 57 (1914).

[3] *Z. anorg. Chem.*, **77**, 377 (1912); *Proc. Nat. Acad. Sci.*, **47**, 441 (1912); *Z. physik. Chem.*, **86**, 513 (1914).

in Fig. 4; the experimental data for these curves will not be given here, but may be estimated approximately from the figure. Wherever three such boundary curves meet there exists a triple point, at which three phases coexist at the invariant temperature and pressure indicated. These triple points are of

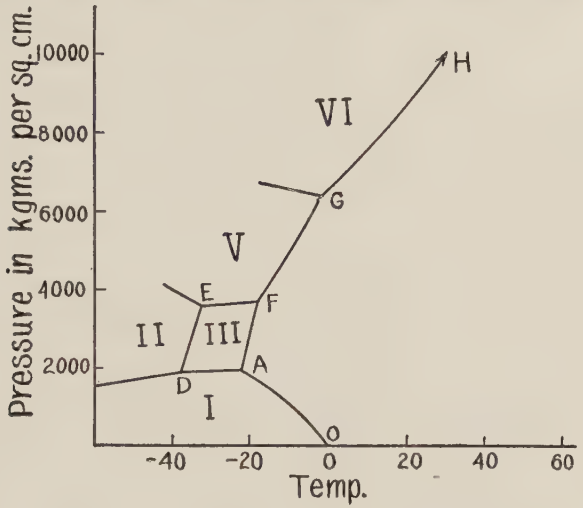


FIG. 5. *p.-t.* Diagram for Water at High Pressures

course all at pressures at which the vapor phase cannot exist, and consist of various combinations of two solid phases with the liquid and of three solids with each other. The entire list of such invariant equilibria is given in Table XIII in the order of increasing pressures, including the triple point for ice water and vapor previously discussed.

TABLE XIII

TRIPLE POINTS IN THE ONE-COMPONENT SYSTEM: WATER

Position in Fig. 5	System	Type	Temperature	Pressure in Kgms. per Sq. Cm.
O	Ice I—liquid-vapor	S_1—*L*—*V*	+ 0.0075	(4.579 mm.)
A	Ice I—ice III—liquid	S_1—S_3—*L*	− 22.0°	2115
D	Ice I—ice II—ice III	S_1—S_2—S_3	− 34.7°	2170
E	Ice II—ice III—ice V	S_2—S_3—S_5	− 24.3°	3510
F	Ice III—ice V—liquid	S_3—S_5—*L*	− 17.0°	3530
G	Ice V—ice VI—liquid	S_5—S_6—*L*	+ 0.16	6380

Of the various univariant equilibria, we will select for qualitative study those in which liquid and a solid are the coexisting phases, indicated by the curves *OA*, *AF*, *FG*, and *GH*. The curve *OA* has already been discussed, and

its inclination toward the pressure axis shown to be in accord with Le Chatelier's theorem. The freezing point is depressed as the pressure is raised until a minimum temperature of $-22°$ is reached at a pressure of 2115 atmospheres. The temperature can now no longer be lowered, whatever the pressure, without causing the liquid to solidify completely; we may therefore consider $-22°$ as the minimum freezing point of water under any set of equilibrium conditions. If we now raise the pressure, a transition of ice I into ice III occurs, and unlike the transition occurring at *O*, it is marked by a decrease in volume; moreover, the new phase, ice III, is denser than water instead of less dense. If we now apply Le Chatelier's theorem, we will deduce that an increase of pressure will raise the freezing point, so that the equilibrium curve for ice III and water must slope upward away from the pressure axis, as shown by the line *AF*. Equilibrium temperatures therefore rise with the pressure until at *F* a new triple point is met and ice III is transformed into ice V by increase of pressure; the new equilibrium curve *FG* has a still more marked slope toward the right until it reaches the triple point *G*, at 6380 kgm. pressure and a temperature of $+0.16°$. At this high pressure the freezing point of water (forming ice V or ice VI, of course, and not ice I) is very close to its freezing point at 1 atmosphere pressure. The equilibrium curve *GH* now inclines still more sharply toward the right, and has been investigated by Bridgman up to pressures of 20,000 kgm., at which the freezing point of water is $+80°$. Of the four equilibrium curves for solid and liquid, but one (*OA*) slopes toward the pressure axis, because the specific volume of ice I is greater than that of liquid water; the other three incline away from the pressure axis, because ice III, ice V, and ice VI have each a specific volume less than that of water.

With this much of specific discussion of the application of the phase rule to water, we may see whether some of the relationships learned may not be given a more generalized treatment. The simple diagram (Fig. 4) may now be looked upon as a diagram for any system of one component in the neighborhood of the triple point for solid, liquid and vapor; the only differences for any system will be in the numerical values of the ordinates and abscissæ, and in the slopes of the three curves. The vapor pressure curve Ot_c will always rise with the temperature, though its slope may be greater or less than that for water, and will extend from the triple point up to the critical temperature and pressure, t_c; it will have a metastable prolongation *OC* which may be either short or long, depending upon the character of the liquid, more particularly upon its viscosity. The so-called amorphous condition of substances is regarded simply as the undercooled liquid in equilibrium with its vapor, as indicated by this metastable prolongation. Such amorphous bodies may show a most astonishing persistence in the metastable condition, even in the presence of the stable form; it is believed that, sufficiently far below the triple point, the rate of transformation becomes very slow because of the viscosity of the liquid and more particularly because of the diminishing number of nuclei from which the crystallization might spread. The vapor pressure curve for the solid, *BO*, will also rise with the temperature in all cases, the rate depending upon the nature of the particular substance. It will lie below the metastable curve *OC*, and will terminate at the triple point *O*, since metastable existence of a solid above its melting point in a one-component system has never been observed. The curve may have one or more transition points upon it at which it changes its direction discontinuously, if the solid exists in several polymorphic forms, just as in the curve *OAFGH* in Fig. 5; a discussion of polymorphism is reserved for a later point in the chapter. The fusion curve *OA* and its continuation may slope upward either toward or away from the pressure axis according as

the solid phase is less dense or more dense than the liquid, and may change its direction at any point, depending upon this relationship. Metastable prolongations of the curve below *O* are unknown. The question as to the further end of the fusion curve is a matter of conjecture. Ostwald believes that it ends in a critical point for the solid-liquid phases, at which the two have the same density and a zero heat of fusion. Roozeboom and Tammann incline to a belief in a much less simple hypothesis, according to which the fusion curve eventually inclines toward the pressure axis and describes more or less completely a closed circle, above which the area for the liquid phase is continuous. Experimental data are not complete enough to give any certainty as to the complete curve.

Treating the diagram of Fig. 4 as a general case, it is instructive to deduce the effect of changes of pressure or of temperature such as can usually be accomplished with little experimental difficulty. Let us consider the changes which will occur if such a system is taken at a temperature below the triple point and a pressure above it, as represented by the point *a* in the diagram, and then subjected to continuous addition of heat while the pressure is maintained constant; the results can all be deduced by following the phase changes along a line of equal pressure, *ab*, called an isobar. At *a* the system consists of solid alone, and addition of heat will bring about no changes except a rise of temperature and an increase of volume until the system reaches a condition represented by the intersection of *ab* with *OA*; here the solid begins to melt, and the temperature remains constant until the solid has completely liquefied. The liquid now rises in temperature again up to the point of intersection of the line *ab* with Ot_c, at which point it begins to vaporize and maintains a constant temperature until the liquid has completely changed to vapor. This evaporation of a liquid at a vapor pressure equal to the total pressure exerted upon the system is the ordinary process of boiling, and the intersection of the line *ab* with Ot_c is the boiling point; since *ab* is drawn at any arbitrary height, it follows that the boiling point is always arbitrarily determined by the pressure under which the system is standing. In ordinary laboratory practice our procedure differs from that sketched above only in that air is usually present either at atmospheric pressure or at a reduced pressure so that vapor of the liquid will be present in the vapor phase within the areas marked *S* and *L* in the diagram. If now the experiment be repeated with *ab* taken at some pressure below the triple point *O*, the changes are fewer; where the intersection with *BO* occurs, the solid vaporizes completely without change of temperature and the process is spoken of as sublimation. If for example the substance taken be solid carbon dioxide and the pressure 1 atmosphere, our second case is exactly described, for the triple point *O* is at a pressure of 5.1 atmospheres and a temperature of $-56.7°$ [1]; the isobar *ab* drawn at 1 atmosphere pressure intersects the curve *BO* at $-78.3°$, at which temperature the solid will remain until sublimation is complete, giving a very simple and convenient method of securing a constant low temperature. Ice, in order to be sublimed without melting, must be maintained under a pressure lower than 4.6 mm., the pressure at its triple point; and iodine, which melts at 114° and a pressure of 91 mm., must be maintained below that temperature and pressure if melting is to be excluded.

[1] Thiel and Caspar, *Z. physik. Chem.*, **86**, 257 (1914).

In the latter case, for laboratory sublimation the process is usually to maintain a constant temperature of 100° at atmospheric pressure, allowing the vapor to diffuse outward until it meets some cool surface upon which it solidifies; this is a process of evaporation rather than sublimation, in that the constant temperature is maintained by the environment whereas in true sublimation the environment is at a higher temperature and the constant and lower temperature of the system is fixed by the pressure and maintained by means of the negative heat of vaporization

The result of changing the pressure at constant temperature can be deduced by following a line drawn parallel to the pressure axis, and called an isotherm, or isothermal line. If, for a system represented by Fig. 4, the isotherm be drawn at a temperature just below the point *O*, the system will be wholly gaseous at low pressures; as the pressure is raised its volume will diminish until when the intersection with the line *BO* is reached the vapor completely solidifies without increase of pressure; when the intersection with the curve *OA* is reached, the solid will melt completely without increase of pressure. If the isotherm is drawn above the point *O*, a single change from vapor to liquid will occur at the pressure of the intersection with Ot_c.

Sulfur: Sulfur is commonly known in two crystalline modifications, rhombic sulfur and monoclinic sulfur; these have a transition temperature (96°) at which they are in equilibrium with each other. Each possesses a melting point, that of the rhombic being approximately 114° and that of the monoclinic about 120°. The liquid form of sulfur undergoes some rather remarkable changes in color and viscosity when heated, and boils at 444.7° C. On rapid cooling of very hot molten sulfur a brownish gum is obtained, called plastic sulfur, which slowly changes into a hard brittle substance, while if sulfur only slightly above its melting point is quickly cooled, the yellow substance is at once formed; these two quickly cooled products differ considerably in their solubility in carbon disulfide, the latter being much the more soluble; they contain varying amounts of a quasi-solid called amorphous sulfur. These are the commonest facts about the substance, which we shall proceed to relate in accordance with the phase rule, although it is only fair to state that by no means all the relationships are known or classified.

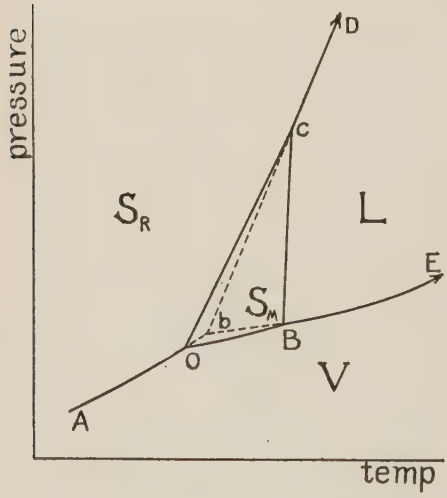


FIG. 6. *p.-t.* Diagram for Sulfur (Schematic)

These relationships are shown qualitatively in Fig. 6. The right-hand part of the diagram (curves *OB*, *BE* and *BC*) will be recognized as nearly

duplicating the diagram for water; *OB* is the sublimation curve for monoclinic sulfur (univariant equilibrium $S_M \rightleftharpoons V$), *BE* is the vapor pressure curve for liquid sulfur (univariant equilibrium $L \rightleftharpoons V$), and their intersection at *B* is the triple point for the invariant equilibrium $S_M - L - V$, the temperature being 120°. *BC* is the fusion curve for monoclinic sulfur; since the solid form is denser than the liquid, as is the case in the majority of instances, the curve slopes upward away from the pressure axis. At *C* there is a second triple point, at which rhombic sulfur, monoclinic sulfur and liquid are in equilibrium; the temperature is 151° and the pressure 1320 kgm. per sq. cm.[1]; the curve *CD* is the fusion curve for rhombic sulfur. For relationships not met with in the study of water we look to the left of the diagram, where we find the curve *AO* indicating the vapor pressure of rhombic sulfur. The point *O* is the transition temperature of the two solid forms, 96°, and is a triple point at which the two solids and vapor are in invariant equilibrium; it is also the point of intersection of the curve *OC*, which is the transition curve of the two solids. Since the two solids coexisting make up a univariant system, it follows that the transition temperature must vary with the pressure. Arguing backward from the diagram to the facts, it may be deduced from the slope of *OC*, by Le Chatelier's theorem, that rhombic sulfur is more dense than monoclinic; the densities are 2.04 and 1.93. The greater slope of the curve *OC* brings about its intersection with *BC* at the triple point *C* already mentioned. This series of curves, if drawn to accord with the experimental data, makes a division of the entire pressure-temperature diagram into four areas, one each for the vapor, liquid sulfur, rhombic sulfur and monoclinic sulfur; the area for the stable existence of monoclinic sulfur, *OBC*, is completely enclosed by the other three.

In addition to the stable equilibria discussed above, there are several metastable equilibria indicated by the dotted lines of Fig. 6. With the metastable vapor-pressure curve of the liquid, *Bb*, we are already familiar from our study of water. In the metastable curve *Ob*, the prolongation of *AO*, is represented the possibility of heating a solid above its transition point into a second solid; this phenomenon is extremely common, and is unquestionably connected with the fact that the rigidity of solids retards the molecular rearrangements necessary for a change in crystalline form. The intersection *b* will be recognized as the metastable melting point of rhombic sulfur, found to be at about 114°, but doubtless with some error, as will appear later. From this melting point, which is of course a triple point, the metastable fusion curve (*bC*) of rhombic sulfur into liquid runs upward to *C*, above which it is continued as the stable fusion curve *CD* mentioned earlier.

The equilibria indicated in the diagram are seen to be numerous. There are four bivariant equilibria, represented in the diagram by areas within which a single phase can exist and within which *both* the temperature and the pressure may be varied; there are six univariant equilibria, represented by lines, indicating two coexisting phases, which may have *either* temperature or pressure varied at will, but not both; and finally there are four invariant equilibria (one being metastable), represented by the points of intersection and indicating that the three coexisting phases can have neither temperature nor pressure altered. The list of univariant and invariant equilibria follows:

[1] Tammann, *Wied. Ann.*, 68, 675 (1899); *Ann. Physik.*, 3, 178 (1900).

TABLE XIV

EQUILIBRIA OF SULFUR

Univariant Equilibria		Invariant Equilibria			
Line	Phases Present	Point	Phases	Temp.	Pressure
AO (*Ob*).....	S_R—V	*O*.....	S_R—S_M—V	96°	
OB.....	S_M—V	*B*.....	S_M—L—V	120°	
EB (*Bb*).....	L—V	*C*.....	S_R—S_M—L	151°	1320 kgm.
BC.....	S_M—L	*b* (metastable)..	S_R—L—V	114°	
OC.....	S_R—S_M				
DC (*Cb*).....	S_R—L				

Passing to a consideration of liquid sulfur, its peculiar properties have been studied and explained chiefly by Alexander Smith [1] and his coworkers, who have established that in the liquid state, as also in the vapor state, sulfur consists of two forms in dynamic equilibrium; to these Smith gave the names sulfur lambda (S_λ) and sulfur mu (S_μ). These differ in their molecular weight, S_λ being of the formula S_8 and S_μ having a lower molecular weight, probably corresponding to S_4. Such dynamic equilibria of liquid or gaseous substances are of course well known; we meet instances in the various cases of tautomerism, and even as simple a substance as water in the liquid state consists of various isomers such as monohydrol (H_2O), dihydrol $(H_2O)_2$, etc., in equilibrium. The peculiarities of the sulfur equilibrium however, to which we may ascribe most of the behavior in which it differs from other substances, are two in number: first, the unusual character of the equilibrium curve, and secondly the relative slowness with which the equilibrium $S_\lambda \rightleftharpoons S_\mu$ is established, making it possible to maintain and study the system in metastable equilibrium by sudden drop in temperature or by use of negative catalysts (SO_2 being very effective) as well as to study true equilibrium mixtures, using positive catalysts such as ammonia, if necessary, to accelerate the attainment of equilibrium. The figures for the composition of liquid sulfur, as obtained by Smith, are as follows; later work by others has given data differing from Smith's by a few per cent only.[2]

TABLE XV

DYNAMIC EQUILIBRIUM: S_λ AND S_μ

Temperature ° C.....	130	140	150	160	170	180	200	220	240	310	448
% S_μ.....	4.2	5.6	6.7	11.0	18.7	22.5	27.0	29.4	33.0	32.6	34.1
% S_λ.....	95.8	94.4	93.3	89.0	81.3	77.5	73.0	70.6	67.0	67.4	65.9

[1] Smith and others, *J. Am. Chem. Soc.*, **27**, 801, 983 (1905); *Z. physik. Chem.*, **42**, 469 (1903); **52**, 602 (1905); **54**, 257 (1906); **57**, 685 (1907); **61**, 200 (1907); **77**, 661 (1911).

[2] For brevity's sake no reference is made here to the existence of the third dynamic isomer, S_π, whose existence has been shown by Aten and confirmed by Beckmann et al. (*Z. anorg. Chem.*, **103**, 189 (1918)). For a bibliography of the work on sulfur up to 1918, see vol. 2, part III of Roozeboom's Die heterogenen Gleichgewichte, issued by Aten in 1918,

When these data are plotted (Fig. 7), it appears that the most rapid changes in composition of the liquid occur between 150° and 200°, and if more narrowly scrutinized, between 160° and 170°. Now, if we consider the contrast in the properties of pure S_λ and S_μ, we shall be in position to understand the striking changes which the liquid solution undergoes at about 160° to 170°. S_λ is light yellow in color, of low viscosity and soluble in carbon disulfide, while S_μ is dark brown in color, quite viscous, and insoluble in that solvent. Liquid sulfur at lower temperatures, consisting largely of S_λ, will therefore have a color and viscosity nearly that of that pure substance; if heated to 160°–170° or above, the considerable increase in the proportion of S_μ gives the liquid its well-known dark color and high viscosity. Let us now assume a mass of molten sulfur at some high temperature, where it contains some thirty per cent of S_μ to be suddenly cooled by pouring into cold water; the proportions are but slightly altered by the change, in accordance with the observed fact that the speed of the reaction is low, and the plastic sulfur thus obtained is a brown viscous gum, which is to be regarded simply as the undercooled solution of the two forms. If it is treated with carbon disulfide, the soluble S_λ is extracted and the residue is undercooled S_μ; it is considered to be the amorphous form of sulfur. Being metastable at these low temperatures, it will in time change into the stable form, which is rhombic sulfur, as shown in Fig. 6. If the liquid chosen for cooling be taken at a temperature below 160°, the proportion of insoluble sulfur present is small, and the material obtained by chilling is chiefly soluble crystalline sulfur. On a theory that the solid phases are not composed of a single form, but are, like the liquid, equilibrium solutions (that is, solid solutions), Smits [1] has suggested a diagram into which all the forms can be fitted.

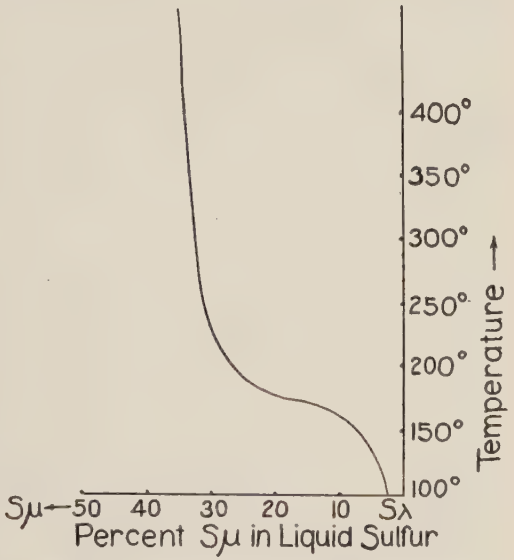


FIG. 7. Equilibrium $S_\lambda \rightleftharpoons S_\mu$ in Liquid Sulfur

The fact of the slow establishment of equilibrium in the liquid phase leads to some important considerations relative to the melting point of sulfur. A melting point is the temperature of equilibrium between the solid phase and the liquid phase, under the pressure of the system. Disregarding the matter

[1] *Z. physik. Chem.*, 83, 221 (1913); also Die Theorie der Allotropie (Barth, 1921). English Translation by Thomas, Longmans, Green and Co., 1923.

of the small effect of substituting atmospheric pressure for the pressure of the system, it is clear that as many as three equilibria may be involved: (1) equilibrium *within* the liquid phase, if it is capable of existing in two or more forms between which changes can occur, (2) equilibrium *between* the liquid phase and the solid phase, and (3) equilibrium *within* the solid phase, if solid solution of two or more forms exists. It is logically a necessity that, while only one equilibrium temperature is possible when all three equilibria have been attained, an indefinite number of temperatures is possible if any one or two of the equilibria have not been reached. Leaving out of consideration, for simplicity, the possibility of metastable conditions in the solid phase, we see that possibilities of complications in the liquid phase may frequently occur. In our study of water it was unnecessary to consider this point, inasmuch as the dynamic equilibrium between monohydrol, dihydrol, etc., is attained instantaneously in the liquid state; liquid water is therefore always in the same condition at a given temperature, and more than a single freezing point (pressure being assumed constant) is not found. But, in the case of liquid sulfur, the liquid phase may have present, according to its history, proportions of S_λ and S_μ widely different from the true equilibrium quantities, because of the slowness with which equilibrium is reached, and the equilibrium temperature with the solid phase, or melting point, may vary from that of pure S_λ in contact with solid to that of a solution containing a large proportion of S_μ. The melting points thus obtained are plotted in Fig. 8. The line *AC* represents the melting point curve for monoclinic sulfur and *DF* that for rhombic. On these curves there are four points of especial interest; these are the two melting points in contact with pure S_λ and S_μ, which have been called the ideal melting points (*A* and *D*), and the two melting points in contact with the true equilibrium proportions of S_λ and S_μ in the liquid phase (*B* and *E*), appropriately named the natural melting points. The curve *BE* is the curve for the dynamic equilibrium in the liquid phase. In Table XVI are given the figures for these melting points as determined by Smith and Carson.[1] It will be observed that these temperatures are sensibly different from those commonly given for the two forms, the discrepancy being greatest in the case of rhombic sulfur.

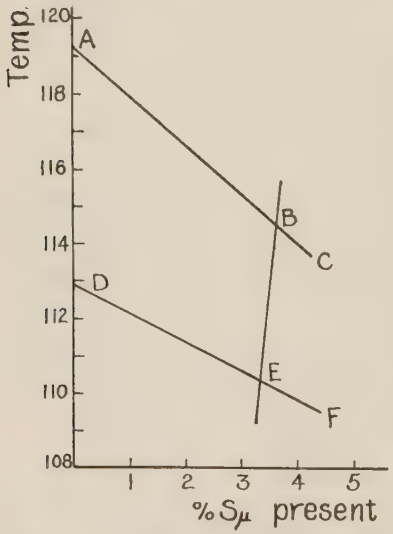


FIG. 8. Melting Point Curves of Monoclinic and Rhombic Sulfur

[1] *Z. physik. Chem.*, 77, 670 (1911).

TABLE XVI

MELTING POINTS OF RHOMBIC AND MONOCLINIC SULFUR

	Ideal Melting Points	Natural Melting Points	S_μ at Natural M.P.
Monoclinic Sulfur.....	119.25°	114.5°	3.6 %
Rhombic Sulfur.....	112.8°	110.2°	3.4 %

A consideration of the above set of facts, depending upon a slow attainment of dynamic equilibrium in the liquid phase, leads to an interesting deduction relative to the number of components of the system. Let it be supposed that in a case of dynamic equilibrium the equilibrium is reached with infinite slowness, that is, that any solution remains perfectly stable and unchanged in its composition; it will follow then that the system is a two-component system, since it will be impossible to express the composition of the liquid in terms of any one substance. Such a system will then have the degree of freedom, or variance, corresponding to a two-component system, that is, one degree of variance higher than if calculated for a one-component system with the same number of phases present; for example, with vapor, solid and liquid present the equilibrium temperature (melting point) is not invariant, but is univariant, varying with the composition. Such would be the case in a system consisting of two isomeric compounds, such for example as ortho-cresol and para-cresol. Now, we have, as a matter of fact, just seen that the melting points of sulfur show just this relation, and we have been treating the system essentially as a two-component system in our latter discussion. A distinction exists here however in that, within reasonable time, equilibrium within the phase is reached, and *once that condition has been attained* the system can be treated as of one component without error; it is therefore spoken of as a pseudo-binary system, since it has, under certain conditions, the properties of a two-component or binary system. It is evident that the distinction between a one-component system (unary system) like water, a two-component system (binary system) like the two cresols, and a pseudo-binary system like sulfur depends upon the speed with which equilibrium is attained within a phase.

In concluding the direct study of sulfur, it should be stated that reference has been omitted to a fourth dynamic isomeride, S_ρ, and to two other metastable solids, S_{III} (nacreous sulfur) and S_{IV}, for the treatment of which the reader is referred to the monographs on the phase rule and the original literature in the journals.

GENERAL CONSIDERATIONS RELATIVE TO ONE-COMPONENT SYSTEMS

Polymorphism: In the discussion of water reference was made to the several solid modifications which have lately been discovered; and in the discussion of sulfur the rhombic and monoclinic forms were considered. These are individual instances of the general phenomenon known as *polymorphism.*

Polymorphic forms are solid phases of the same ultimate composition, differing among themselves in crystalline form, free energy and other physical and chemical properties, but yielding identical liquid or gaseous phases upon fusion or evaporation. In cases where the polymorphic forms are composed of a single element (sulfur, phosphorus, carbon, tin, etc.), it is usual to speak of the forms as allotropic, while if the forms are of compound composition, as is the case with ammonium nitrate, silver nitrate, mercuric iodide, etc., the general class name is used; allotropism is therefore simply a special case of polymorphism. Every polymorphic form exists as a separate phase, and the number of solid phases for a single component is therefore the number of polymorphic forms existent. By the application of the definition given we can clearly differentiate polymorphism from isomerism; in the latter case, we have differing solid modifications of the same composition which however continue to maintain

their differences in the liquid or gaseous state, and any system made of isomers is therefore a two-component or multi-component system, since the phases cannot have their composition expressed by less than two terms.

With the question as to the ultimate condition in polymorphic solids the phase rule is not concerned; the difference may lie in the geometrical arrangement of the molecular units making up the crystals, in the molecular weight, or possibly in the proportions of different molecular species existing in dynamic equilibrium.[1] It is the interrelationships of these forms, as separate phases, that the phase rule is in position to classify. In many cases, of which sulfur is one, it has been found that two polymorphic forms possess vapor tension curves which approach each other with alterations in the temperature, intersecting at a point (called the *transition point*) at which the vapor pressures are identical. At such a transition temperature, and only there, are both solid phases stable; here an equilibrium exists between them such that addition of heat will effect a transformation into the form stable at higher temperatures, without however raising the temperature until the other form has disappeared, since the change is at an invariant point (triple point). Abstraction of heat brings about the reverse change, also at constant temperature. Polymorphic forms, which stand in the relation of possessing such a transition point at which they are in equilibrium, are known as *enantiotropic forms;* enantiotropy has been illustrated in the study of water and of sulfur and is frequently met with. Tin offers an interesting example of this sort, possessing a transition temperature of 18°, above which the stable form is white and has a density of 7.24, and below which the stable form is gray and has a density of 5.8. Not only many metals, but many compounds, such as ammonium nitrate, silver nitrate and mercuric iodide, exist in enantiotropic forms.

In other instances of polymorphism, the vapor pressure curves of the two forms do not meet; such forms, which lack a transition point, are called *monotropic.* It follows that under all conditions where both can exist, the one form is always stable, and the other is always metastable. The metastable form always has the higher vapor pressure, and will therefore change into the stable form by a process of distillation such as was illustrated in the case of undercooled water and ice; the rate of such a change may however be almost infinitely slow, especially where the actual vapor pressures are very small. An example of monotropism is found in the case of phosphorus; white (or waxy) phosphorus is metastable with respect to red phosphorus and possesses a higher vapor pressure at all temperatures up to its melting point, 44.1°; at room temperature, however, its rate of change into red phosphorus is extremely slow, so that the common method of preparing the red variety from the yellow consists in using high temperatures such as 250–300°, at which equilibrium is much more quickly obtained, and the vapor formed from the liquid yellow variety may condense as red phosphorus. In other cases it is not easy to determine whether a given form is monotropic or enantiotropic; thus, in the case of

[1] For discussion, see Smits, Die Theorie der Allotropie (Barth, 1921); translated by Smeath Thomas (Longmans, Green and Co.).

carbon, graphite is known to be the stable form at very high temperatures and diamond the unstable, but decisive experiments have not been performed to determine whether or not there is a transition point at some temperature below 1000°. Whichever is the stable form at low temperatures, the rate of transformation is infinitely slow, which is by no means incredible at temperatures so far below the melting point. If there is a transition point not yet found, the two forms of carbon would then be considered as pseudomonotropic rather than truly monotropic.

With this added knowledge as to polymorphic solid forms, a brief re-inspection of Figs. 4, 5, and 6 will lead to a simple but useful generalization. It will be observed that the equilibrium curve for any phases indicated is always continuous; discontinuity in direction occurs only where two or more curves intersect, that is, where an increase in the number of phases occurs. The newly appearing phase may be vapor, liquid, or any solid polymorphic form. In experimental work the appearance of a discontinuity in any type of equilibrium curve is a sure sign of a change of phase, and demands search for and identification of the new phase; the rule applies not only for one-component systems, but equally for those of more than a single component.

Condensed Systems: In the case of equilibria between solid phases and liquid phases (solubility, freezing points, etc.), the effects of moderate changes in pressure are very small, and in many cases may be ignored. Thus, the freezing point of water under its own pressure and under one atmosphere pressure differ by only 0.0075°, an amount which is not of significance in most measurements.

Such systems, consisting of solid and liquid phases only, are called *condensed systems*, and we may therefore treat condensed systems as independent of the pressure within moderate limits. This is a matter of much convenience in experimental work. In treating a condensed system, therefore, we may work either under some constant pressure, sufficiently high to prevent the formation of a vapor phase, or, as is more commonly done, work with open vessels under the atmospheric pressure, ignoring the fact that the pressure is not the true equilibrium pressure of the system and likewise ignoring the presence of the air as an additional phase, as has been discussed with respect to the triple point for water; the error involved by so doing is usually less than the experimental error in determining the temperature or in measuring the solubility.

Liquid Crystals:

Beginning with a discovery by Reinitzer [1] in 1888, a number of organic compounds have been observed to undergo changes upon heating which cannot be reconciled with the theory that pure substances exist only as vapors, liquids, and polymorphic solids. When solid cholesteryl acetate, which Reinitzer investigated, is heated, it apparently melts sharply at a given temperature, giving rise to a substance that possesses the most obvious properties of a liquid; that is, it possesses fluidity, and will form droplets if suspended in another liquid of equal density. On the other hand, it possesses certain properties hitherto only observed in solids; it is turbid or milky in appearance, and (most important of all) is *anisotropic*, showing double refraction and giving interference colors on examination by polarized light. At a higher temperature a second transition point is reached, at which the peculiar substance changes to a liquid of entirely normal character.

The effort to explain such substances as emulsions or similar heterogeneous systems has not been successful, and they have been accepted as constituting a new type of phase and are called liquid crystals. Their classification as "crystals" is justified because of their

[1] *Monats.*, 9, 435 (1888).

showing properties which depend upon a regularly orientated internal condition; such are the anisotropic behavior referred to above, the existence of a space-lattice structure as shown by X-ray analysis [1] in the case of *p*-azoxyanisole, and the possession of a perfectly definite transition point (or melting point) into normal liquids, which melting point is affected by pressure or the presence of a second component in the same fashion as the melting point of unquestioned solids.[2] The belief that the liquid crystals are heterogeneous could not be maintained after it was shown that the turbidity is only apparent, being due to diffraction caused by differently oriented crystals and vanishing upon examination of the smaller units in the field of the microscope; indeed, liquid crystals have been prepared [3] which fail to show any turbidity when examined by unaided vision.

Viewing the liquid crystals as an independent type of phase, they may be fitted into the phase-rule diagram as shown in Fig. 9. The point *O* represents the triple point for solid, liquid crystals and vapor, and is called simply a transition point without any new specific name; the point *B* is the triple point liquid crystal + liquid + vapor, and is named the melting point, being entirely analogous to the melting point as usually defined. In Table XVII are given the data for several illustrations. It should be stated however that the study of liquid crystals is not yet complete enough so that a perfectly general treatment can be made which will fit the liquid crystals as a stable or metastable phase into all one-component systems, as can be done with the solid, liquid and vapor phases.

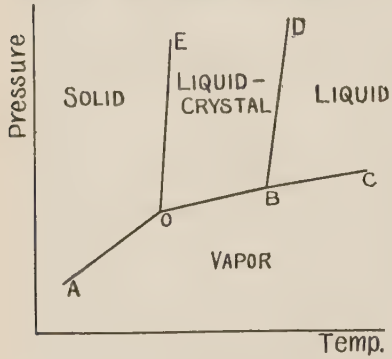


FIG. 9. One Component System including Liquid-Crystal Phase

TABLE XVII

TRIPLE POINTS FOR LIQUID CRYSTALS

Substance	Transition Point *O*	Melting Point *B*
Cholesteryl benzoate	145.5°	178.5°
p-Azoxyanisol	118.3°	135.9°
p-Azoxyphenetol	134.5°	168.1°
Condensation product: benzaldehyde + benzidine	234°	260°
Azine of p-oxyethylbenzaldehyde	172	196
Condensation product: p-tolylaldehyde + benzidine	231	—
p-Methoxy cinnamic acid	169°	185°

Suspended Transformation: Suspended transformation has been referred to in the instance of the undercooling of liquid water, as represented in Fig. 4 by the curve *OC*, and in the case of sulfur (Fig. 6) suspended transformation

[1] Lingen, *J. Franklin Inst.*, 191, 651 (1921); 192, 511 (1921).

[2] For a bibliography of the extensive researches on liquid crystals, see Findlay's Phase Rule, 6th Edition (1923), p. 65.

[3] Vörlander and Kasten, *Ber.*, 41, 2033 (1908).

is indicated by the curves *Ob* and *Bb*. In general, where a series of coexisting phases can be maintained in metastable equilibrium, that is, under conditions where complete representation of the system shows that a different combination of phases, pressures and temperatures is the stable arrangement, the system is said to show suspended transformation. The ease with which such a condition may be obtained or the persistence with which it may be maintained depends upon the general physical and chemical nature of the system as well as upon the particular phase reaction which has been suspended, and no entirely general treatment of the condition is yet possible. The suspended transformation, liquid → solid, is perhaps most commonly met and has been most fully studied.

Tammann [1] found that the crystallization, the occurrence of which ends the condition of suspended transformation, does not occur throughout the whole mass at once, but proceeds from one or more points that may be looked upon as nuclei. It is found that the number of such nuclei appearing per unit time in unit mass of the liquid increases at first with the degree of undercooling, reaches a maximum at some temperature and then decreases. The rate of crystallization not only depends upon the number of such nuclei, but is also dependent upon the passive resistance which the liquid offers to the propagation of the branches of the crystalline material; this passive resistance becomes greater as the temperature falls and the liquid becomes more viscous. At temperatures sufficiently below the melting point the number of nuclei will be small and the rate of crystallization enormously slow, so that the suspended transformation may continue almost indefinitely. This is the condition existing in the so-called amorphous solids, which are greatly undercooled liquids of high viscosity showing suspended transformation. Considering other types of suspended transformation, the change solid → liquid has not been observed to show such a condition in any one-component system. The transition solid → solid may be made to show suspended transformation either with rising or falling temperature or with rising or falling pressure; indeed the rigidity of the solid state is a property most favorable to slow transformation. The reactions liquid ⇌ vapor and solid ⇌ vapor in both directions are very liable to suspended transformation, as witness the phenomena of superheating of liquids and the undercooling of vapors which occur where nuclei of all sorts are carefully excluded. In general, suspended transformation is most easily limited or ended by introduction of a nucleus of the specific phase with respect to which the system is metastable, e.g., the missing solid for an undercooled liquid; but, as has been shown, the change may even then be indefinitely slow. Thus calcite has been shown to be the stable form of calcium carbonate under terrestrial conditions, but the occurrence in nature of the metastable form, aragonite, is sufficient indication of the slowness of the transformation.

Experimental Methods for One-Component Systems: Space is not here available for discussing experimental methods in detail. Transition temperatures of two solids are most commonly determined by dilatometrical methods; i.e., by observing the change of volume of a solid with rise or fall of temperature, which will upon being plotted give a smooth curve up to the transition temperature, at which there is an abrupt change of volume with the formation of the new phase with its entirely different density. The transition temperature solid ⇌ liquid is more commonly determined by thermal methods, that is, by subjecting the system to the influence of a constant higher or lower temperature, which causes a regular increase or decrease of temperature to occur until the equilibrium temperature is reached; at this point the latent heat of fusion will hold the temperature constant until the change is complete. In the use of

[1] *Z. physik. Chem.*, **25**, 441 (1898).

these, or any other of the many methods, suspended transformation must be prevented or compensated.

Systems of Two Components

In passing to the study of systems classified as of two components, it will be well to consider briefly certain general facts as to the components, independent variables, and phases. As previously stated, a system belongs to this class if it is possible to express the composition of all the phases in terms of two substances, and not less than two. The haphazard choice, however, of any two pure elements or compounds from the laboratory shelves may not be depended upon to give merely a two-component system, but may also give rise to three-component systems, depending upon the nature of the substances taken. If the two substances employed give rise to no phases except such as are intermediate in composition between the two substances taken, the system will conform to the requirements for a two-component system; thus, the formation of solutions, which are always intermediate in composition between their components, introduces no new complication, nor does the formation of any *additive* compound from the two substances. Sodium sulfate and water, for example, may form, in addition to phases composed of the simple constituents, a solution of the two and may also form several hydrates, such as $Na_2SO_4.10H_2O$; the system is of two components, by application of the rule. If, on the other hand, the two substances form compounds other than those of an additive nature, the system cannot be regarded as of two components; e.g., bismuth nitrate and water form by hydrolysis phases consisting of basic nitrates, such as $Bi_2O_3.N_2O_5.H_2O$, whose composition cannot be expressed in terms of bismuth nitrate and water nor of any other two substances derivable from them; the system is, therefore, of three components.

The independent variables in two-components systems are three in number, instead of the two considered in the case of one-component systems; in addition to the pressure and temperature, the composition of phases may also vary independently, through the formation of solutions. In order to make a complete representation of these three variables graphically, it is necessary to use diagrams in three dimensions, leading to surfaces and volumes in addition to the points, lines and areas occurring in two-dimensional representation. However, it is possible to study many of the relationships satisfactorily in two-dimensional graphs by choosing two of the three variables for representation, where the third is assumed constant or ignored because of its quantitatively small effect upon the equilibria. We shall therefore represent the conditions in this section by use of the three possible two-variable combinations, giving what are spoken of as p–t diagrams, p–c diagrams and t–c diagrams, where p, t and c stand respectively for pressure, temperature and composition.

In two-component systems we meet with a type of phase not occurring in one-component systems, namely, the *solution* phase. It lies in the nature of elementary instruction in chemistry that the student should in his introduction to chemistry obtain a somewhat restricted view of solutions; it lies in the phase

rule to make clear how the term is of very broad significance, including many substances which may appear to be quite different. van't Hoff[1] has given a most satisfactory definition of the term solution: a solution is any phase the composition of which may vary continuously within certain limits. That a solution is a phase, and therefore homogeneous, excludes at once all mixtures, which are necessarily heterogeneous; that it may vary continuously in composition excludes elementary substances and compounds, each of which has definite composition. Such a classification of bodies into mixtures, elements, solutions and compounds is based upon homogeneity and composition and not upon the physical properties upon which the physicist's classification into solids, liquids and gases is made. Solutions may further be given a secondary classification on the basis of the physicist's three states of aggregation; there may be gaseous solutions, liquid solutions, and solid solutions. Gaseous solutions occur whenever any two gases are brought together, since all gases show unlimited solubility (a term to be defined later); liquid solutions are known popularly as well as by the chemist, and the term is applied to any homogeneous liquid where composition may be made to vary continuously, whether it has been prepared from a solid and a liquid like salt and water, a gas and a liquid like carbon dioxide and water, or substances in any initial physical state; and solid solutions, although less commonly met with, exist wherever the homogeneous phase has assumed a solid condition, as in the iron-carbon alloy known as steel. It is with these various types of solutions that we shall find our principal interest in the study of two-component systems.

By application of the phase-rule equation, it follows that for two-component systems, four coexisting phases give rise to invariant equilibrium, three coexisting phases to univariant equilibrium, two coexisting phases to bivariant equilibrium, and one phase to trivariant equilibrium. Trivariance is here

TABLE XVIII

EQUILIBRIA IN TWO-COMPONENT SYSTEMS

Two-phase Equilibria (bivariant)	Three-phase Equilibria (univariant)	Four-phase Equilibria (invariant)
$V - L$	$V - L_1 - L_2$ $V - L - S$	$V - L_1 - L_2 - S$ $V - L - S_1 - S_2$, $V - L_1 - S - L_2$
$L_1 - L_2$	$L_1 - L_2 - V$ $L_1 - L_2 - S$	$L_1 - L_2 - V - S$ $L_1 - L_2 - S_1 - S_2$, $L_1 - L_2 - S - V$
$L - S$	$L - S - V$ $L_1 - S - L_2$ $L - S_1 - S_2$	$L_1 - S - V - L_2$, $L - S_1 - V - S_2$ $L_1 - S - L_2 - V$, $L - S_1 - L - S_2$ $L - S_1 - S_2 - S_3$, $L - S_1 - S_2 - V$
$V - S$	$V - S - L$ $V - S_1 - S_2$	$V - S - L_1 - L_2$, $V - S_1 - L - S$ $V - S_1 - S_2 - S_3$, $V - S_1 - S_2 - L$
$S_1 - S_2$	$S_1 - S_2 - L$ $S_1 - S_2 - V$ $S_1 - S_2 - S_3$	$S_1 - S_2 - L - V$, $S_1 - S_2 - L_1 - L_2$ $S_1 - S_2 - V - L$, $S_1 - S_2 - V - S_3$ $S_1 - S_2 - S_3 - S_4$, $S_1 - S_2 - S_3 - L$, $S_1 - S_2 - S_3 - V$

[1] van't Hoff, *Z. physik. Chem.*, **5**, 323 (1890).

possible, since variations in composition may occur in addition to variation in pressure and temperature. Of gaseous phases there can never be more than one present; of liquid phases, two is the maximum number thus far observed in coexistence; and of solids, there may coexist any number possible under the statement of the phase rule, consisting of pure components in their various polymorphic forms, of additive compounds, or of solid solutions. The number of possible equilibria is too great to admit of complete study in this chapter; the following table gives in the first column the five possible types of bivariant (two-phase) equilibria, which by formation of a third phase give rise to the univariant equilibria of column 2, and by addition of a fourth phase the invariant equilibria of column 3. The number of such types of phase complexes is here calculated with the restriction that the coexisting phases cannot include more than one vapor phase, nor more than two liquid phases. In columns 2 and 3 occur many repetitions of phase complexes; the total number of different systems is seventeen, of which five are bivariant, six univariant and six invariant.

The classification given shows the number of equilibria. The number of specific equilibria in a given system may, however, be much larger through the occurrence of many different solid phases; thus the univariant type equilibrium $V - L - S$ may occur in as many specific forms as there are solid phases possible to be substituted for S. In our study of these extensive possibilities our method will be to consider each of the five bivariant equilibria in turn, with such of the univariant and invariant equilibria derivable from them as have special interest.

A. The Equilibrium; Gas-Liquid

The equilibrium between a gas and a two-component liquid, known as a binary solution or less happily as a binary mixture,[1] has a variance of two; the vapor pressure of such a system therefore depends upon the composition if the temperature be kept constant, or upon the temperature if the composition be kept constant. If the two components possess unlimited mutual solubility, the composition may be made to vary from 100 per cent of one component to 100 per cent of the second, and a continuous vapor pressure curve at constant temperature may be drawn. The dependence of this vapor pressure upon the composition of the liquid, at a constant temperature, has already been discussed in Chapter VII. In an ideal solution the vapor pressure relations will follow Raoult's law, and the total pressure of the two components on a pressure—composition diagram falls on a straight line connecting the pressures of the two components; in the more common cases where the solution is not ideal and Raoult's law does not express the facts, the total pressure will vary from this

[1] The use of the term "mixture" for a homogeneous solution is to be deplored, since it is a term implying heterogeneity, and therefore confuses the essential phase relations. In this chapter effort will be made to avoid the use of the word mixture and all its derivatives except where heterogeneity is actually present; on account however of prevalent usage, it will occasionably be necessary to refer to the less desirable nomenclature.

straight line, being greater than the ideal for some solutions and less than the ideal for others. In all cases however it is found that the liquid phase is different in composition from the vapor phase, except in the case where the vapor pressures of the two components are identical and at maximum and minimum points, discussed later.

The Distillation of Binary Solutions: Relations of much practical interest are found if one studies the equilibrium gas-liquid at constant pressure instead of constant temperature. With two phases present and the restriction added

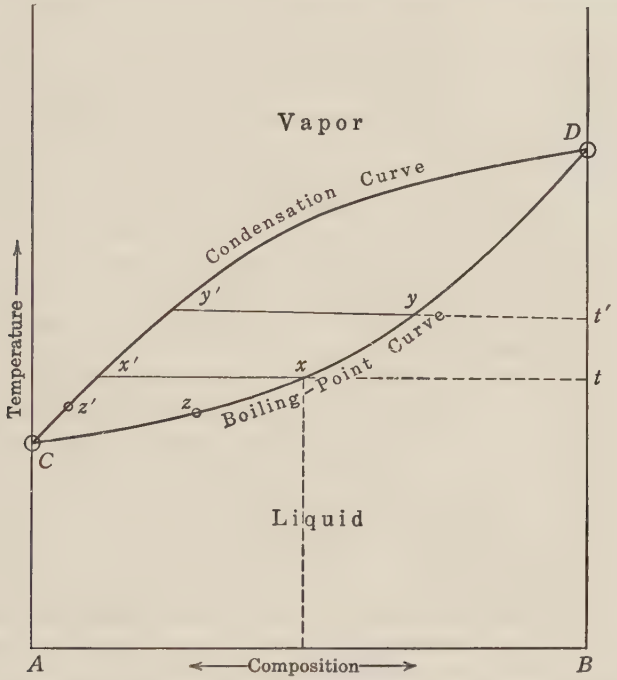


FIG. 10*a*. Boiling-Point Diagram for Liquid-Vapor Equilibrium, Two-Component System

that the pressure be kept constant, such a system is univariant and we may plot the relation of the boiling point temperatures to the composition, as shown in Fig. 10*a*. The point *C* represents the boiling point of component *A*, that is, the temperature at which its vapor pressure is equal to that of the environment, usually the atmospheric pressure; *D* is the boiling point of component *B*. The upper curve represents the composition of the vapor phase and the lower curve that of the liquid phase; as has been previously stated, these two phases are commonly not the same in composition at equilibrium. If we take a liquid composed of 50 per cent each of *A* and *B*, its boiling point will be represented by the point *x* on the lower curve; the vapor which it will give off, necessarily at the same temperature, is represented by the point *x'*;

the line connecting these two points is called a *tie-line*. It will be seen that we are now cataloging the data upon which a fractional distillation depends, namely the boiling point of a binary solution, and the composition of the gaseous and liquid phases in equilibrium at that temperature. The theory of such a fractional distillation is simple, though the execution may be quite otherwise. The first vapor which is given off, of the composition x', is obviously richer in A than was the original liquid x, that is, richer in the lower-boiling component. As the distillation is continued, the removal of this material leaves the residual liquid phase richer in B, and therefore necessarily of a higher boiling point; if the vapor is continuously removed the composition of the liquid phase passes along the lower curve from x to y while that of the gaseous phase, which is the distillate, passes along the upper curve from x' to y', while the boiling point has risen from t to t'. If we interrupt the distillation at this point, we will have a first fraction of distillate of a composition representing the average of x' with y', and as will be seen, distinctly richer in A than was the original liquid. By making the cuts into fractions at suitable temperatures, and repeating the operation with each fraction thus obtained, the separation may be made more and more complete and finally samples approximating to pure A and pure B may be had, their purity being established by the fact that each may be distilled completely at a constant temperature (C and D respectively) and not with a rising temperature as with the original two-component solution.

In actual practice however the conditions are not so simple as those outlined. The vapor phase and the liquid phase do not finally part company at the surface of the liquid in the distilling vessel, but at the point where the condenser is set into its neck; because of the cooling effect of the outside temperature, the ascending vapors are necessarily at a lower temperature at this outlet than when leaving the boiling liquid. Referring to Fig. 10*a*, the vapor passing into the condenser will not have the temperature and composition x', but a lower temperature and different composition represented by z'; if equilibrium is established at this point, the liquid here running down the sides of the distilling flask will have the composition z. Between the exit tube and the surface of the liquid there is therefore present at the initial moment a series of vapors represented along the line x'–z', and a series of returning liquids represented along the line x–z, so that the average composition obtained between the temperatures t and t' is to some extent altered. Further, there is introduced the whole question as to whether the system undergoing distillation is truly at equilibrium. The usual operation which we call boiling or ebullition is a superheating phenomenon, and the formation of visible bubbles in the liquid at the surfaces where heat is applied is convincing evidence of the superheating; the more violent the superheating is, the larger the bubbles become, and the greater the chance that they will escape before coming to equilibrium with the liquid phase. A true distillation in which there is no superheating will proceed only so fast that the latent heat of vaporization at the surface of the liquid will suffice to keep the temperature from rising above the true equilibrium temperature; vapor will then be lost only at the surface, and the operation will be as

free from visible effects as an ordinary evaporation; in fact, it is in no sense different from an evaporation, except that the pressure of the vapor escaping is by definition equal to that of the environment. This question of equilibrium, here discussed with reference to the main mass of the liquid in the distilling vessel, is of course to be met with at every stage as the vapor travels up the neck of the vessel. In order to insure conditions of equilibrium, various types of distilling heads have been devised, the general purpose of which is to secure as intimate contact as possible between vapor and liquid at all heights in the apparatus until the vapor passes into the condenser. The student interested in the practical operation of fractional distillation should not fail to consult Young's book [1] on that topic.

Minimum and Maximum Boiling Points: It has been found that many binary liquids, and perhaps the majority of them, can be represented by the curves of Fig. 10*a*. However, there are many cases known in which these curves show a minimum boiling point, and a smaller number of cases in which a maximum point exists. These two conditions will correspond of course to the cases where the vapor-pressure curves show a maximum and minimum point respectively, the systems possessing a maximum on the vapor-pressure curve showing a minimum on the boiling point curve, and vice versa. We will consider the case where a minimum in the boiling point curve exists, as in Fig. 10*b*. The condensation curve will be above the boiling point curve at all points except at the minimum point, where the two curves meet; failure of the gas curve to meet the liquid curve at this point can be shown mathematically to represent either that the vapor curve is discontinuous, meaning the appearance of an additional phase which is non-existent, or that liquid can exist with no gas phase possible of equilibrium with it, which is an absurdity. At this minimum point, marked E, the two phases are of the same composition, and it follows therefore that if a solution of this composition be taken for distillation, the distillate and the residual liquid will have identically the same composition throughout the distillation. Such solutions which distill without change in composition or variation in temperature have been called azeotropic solutions. If any other composition be taken for distillation, as x, the same logic may be applied to it as in the case previously discussed; by repeated fractionation, the material may be separated into two parts, one having the composition D and the other the composition E. The fraction of composition E obviously cannot be so fractioned as to change its composition toward C, since it boils without alteration. In such cases then no single sample can possibly be so fractioned as to give the two components, A and B, but only so as to give A with the azeotropic solution or B with azetropic solution, dependent on the composition taken for distillation. The effect of this limitation on fractional distillation is important. Thus, in the case of ethyl alcohol and water, shown in Table XVIIIA, an azeotropic solution exists containing 4.43 per cent water and 95.57 per cent alcohol. If a dilute alcoholic solution is fractionally distilled, it follows that it cannot be concentrated above 95.57 per cent however effective the fractionating

[1] Sidney Young, Distillation Principles and Processes, Macmillan and Co., London, 1922.

apparatus; the commercial alcohol, as is well known, is of approximately this composition. A few other examples of this class are given in the first part of the table.

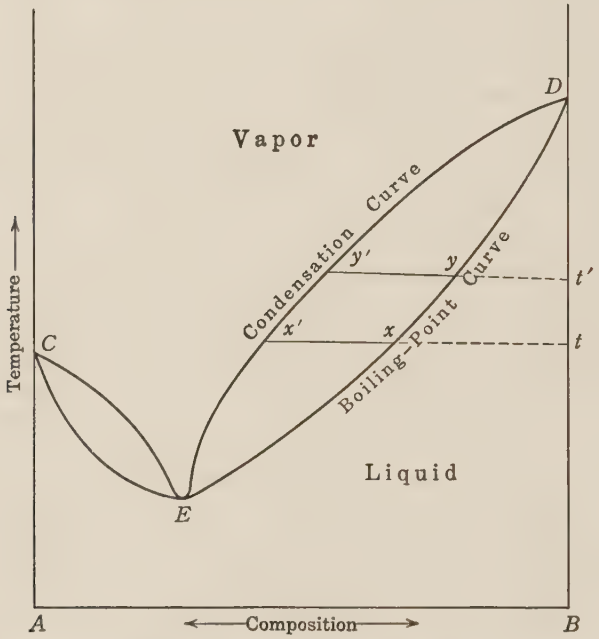


FIG. 10b. Boiling-Point Diagram; Two-Component System with a Minimum Boiling-Point

TABLE XVIIIA

BINARY AZEOTROPIC SOLUTIONS (1 ATMOSPHERE PRESSURE)

1. *Solutions with Minimum Boiling Point*

A	*B*	B.P. of *A*	B.P. of *B*	B.P. of Solution	%*A* in Solution
Water	Ethyl alcohol	100	78.3	78.15	4.43
Ethyl alcohol	Chloroform	78.3	61.16	59.4	7.00
Ethyl alcohol	Ethyl acetate	78.3	77.15	71.8	30.98
Benzene	Cyclohexane	80.2	80.75	77.5	55.

2. *Solutions with Maximum Boiling Point*

Water	Nitric Acid	100	86.	120.5	32.
Water	Hydrochloric acid	100	−84.	108.5	79.76
Phenol	Aniline	181.5	184.35	186.22	42.
Acetone	Chloroform	56.4	61.2	64.7	20.

Still another set of conditions is represented by the latter part of Table XVIIIA—systems with a maximum boiling point. Fig. 10*c* represents such cases Here the fractionation of any solution x leads to an azeotropic solution E—much more readily obtained than in the case of Fig. 10*b*, since here any solution, if continuously boiled, must eventually come to the composition E, whereas in the former case the residue becomes either D or C; all three cases are alike in that the residue inevitably becomes the liquid of highest boiling point attained by continuous upward movement upon the boiling point curve. Because of the ease with which such azeotropic solutions with maximum boiling

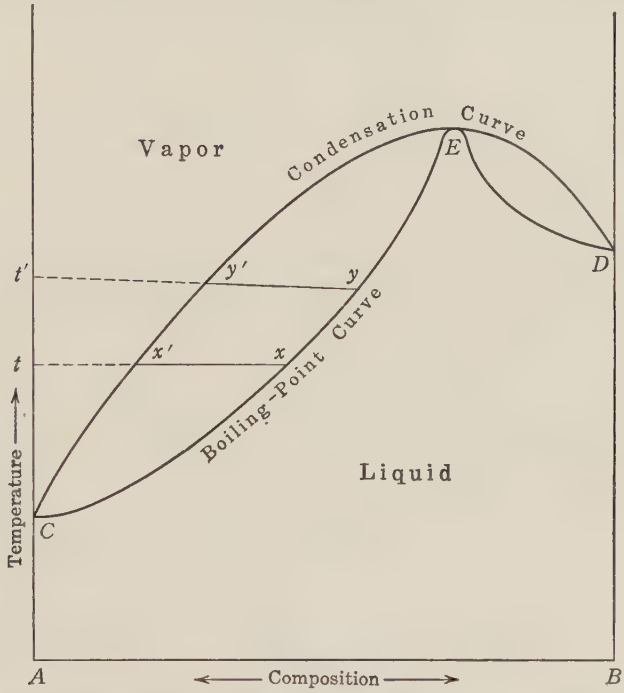


Fig. 10*c*. Boiling-Point Diagram, Two-Component System with a Maximum Boiling-Point

point are obtained from aqueous solution of certain common acids, they have long been known. The commercial concentrated nitric acid will be seen to be the azeotropic solution of Table XVIII-A. In the case of hydrochloric acid solutions, Hulett and Bonner [1] showed that the azeotropic solution could be prepared with high accuracy and used as a reliable acidimetric standard; at 760 mm. pressure the boiling point is close to 108.5 and the solution contains 20.24 per cent HCl. The corrections for small variations in barometric pressure were measured.

[1] Hulett and Bonner, *J. Am. Chem. Soc.*, **31**, 390 (1909).

Since azeotropic solutions have a constant composition, unchanged by distillation, it was at an early date thought that they constituted *bona fide* chemical compounds—a mistake analogous to that made with respect to eutectic mixtures, to be discussed later. The refutation of this claim lies in the fact that, if the pressure be varied, another azeotropic composition is found in every case; in other words, the composition is a function of the pressure, and is not fixed and definite.

With reference to Figure 10*a*, 10*b* and 10*c*, it should be noted that the three types of curves are identical with those shown later in Fig. 23 for solid solutions, and that the theory of fractional distillation is essentially the theory of fractional precipitation where solid solutions occur; in both cases we are dealing with equilibrium between two phases, each of which is a solution and therefore continuously variable in composition.

If a system, gas-liquid, is submitted to such conditions that a second liquid phase appears, there are features of interest in the new univariant equilibrium which results ($V - L_1 - L_2$). Leaving to a later section a more complete discussion of the limited or restricted solubility that must characterize the liquids, let us simply assume that we have such a pair of liquids in equilibrium with their vapor, and let us keep in mind that each of the liquids contains both components, since it is an empirical rule that solubility of liquids, if it occurs at all, is always mutual. In Fig. 10*d* is given a $p - c$ diagram of such a system, in which we assume a constant temperature; the varying compositions are shown on the axis AB and the pressures on the ordinate AC. The vapor pressure of the pure component A is represented by the point C. Let us assume that addition of component B lowers the total pressure of the system; if, as sometimes happens, the total pressure increases instead of diminishing on addition of B, the detail only of the diagram will differ from Fig. 10*d*, the essentials remaining the same. The curve CE is then a part of the curve of the total vapor pressure of the system. At the point E we reach the saturation concentration of the liquid, represented by the composition x, and further addition of B gives rise to a new liquid phase of the composition y. We now have two liquid phases and vapor at a fixed temperature, and the system is isothermally invariant; that is, no changes in pressure or composition can occur so long as the temperature is kept constant and the three phases are retained. Addition of B therefore increases only the mass of the second liquid y. Turning attention to the vapor pressures, since the liquid x, the liquid y and vapor are in equilibrium with each other, the liquid

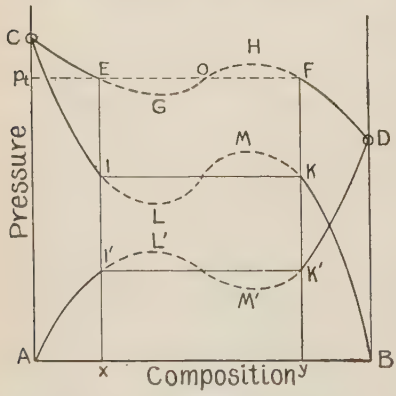


Fig. 10*d*. *p.-c.* Diagram for Liquid-Vapor Equilibrium, Two Component System, Two Liquid Phases

y must have the same vapor pressure as x, namely p_t; both its pressure and composition are therefore fixed by the point F. Any relative quantities of A and B taken so as to give a total composition between x and y can give only x and y as solutions and a total pressure p_t. When the amount of B is increased so that the composition falls to the right of y, the phase x disappears and the vapor pressure falls along the curve FD, which terminates at D, the pressure of the pure component B. The total vapor-pressure curve therefore consists of two discontinuous parts, CE and FD, connected by a line of invariant pressure. In the metastable region $E - F$ the curve is believed to exhibit a minimum and maximum (G and H) and a point of inflexion O, like the pressure-volume curve for a pure liquid below its critical temperature, as shown by van der Waals; using the reasoning made familiar there, the curves EG and HF are to be regarded as metastable and GOH as unrealizable. The familiar theory of van der Waals, as applied to a pure liquid, has been extended so as to cover the case of a binary liquid solution.[1] The complete curve here drawn is the curve for the composition of the liquid phases; that for the composition of the vapor phase, which would fall below $CE - FD$, is not here indicated.

Passing to the partial pressures of the individual components in the system, the curve for the partial pressure of A must begin at C and must reach the level of zero pressure when A is absent, that is, must end at B. The interrupted curve CI–KB shows its course. The points I and K possess special interest. The vapor pressure of A in the solution x must be the same as in the solution y, since otherwise a distillation from phase x to phase y would occur. It follows then that the pressure of A in the phase in which it predominates (x) is in nowise different from its pressure in the phase in which it is present in but small amounts. This fact becomes still more striking if one considers pairs of liquids in which the mutual solubility is very low, as in benzene and water; here, the solubility of water in benzene at 25° is only .07 per cent [2] and that of benzene in water is of the same order, so that the points x and y very nearly coincide with A and B; yet the vapor pressure of benzene in the phase containing only about 0.1 per cent benzene is exactly equal to that in the phase containing 99.93 per cent benzene, that is, practically as high as that of pure benzene. This was first demonstrated experimentally in the case of ether and water by Konowalow.[3]

It is of value to keep this relationship in mind, so that the error may not be made of carrying over into the realm of concentrated solutions ideas based upon the theory of dilute solutions, according to which the vapor pressure is lowered in proportion to the molecular concentration of the second component. Expressing the condition in the general language of Gibbs' concept, the chemical potential of a component in two phases at equilibrium is the same in the dilute phase as in the concentrated phase.

What has been said for the curve CI–KB applies equally to the partial pressure curve for B, namely DK'–$I'A$. The metastable and labile sections between I and K and between I' and K' represent the same conditions as in the curve for total pressures.

[1] van der Waals and Kohnstamm: *Lehrbuch der Thermodynamik*, 1800.
[2] Hill, *J. Am. Chem. Soc.*, **45**, 1154 (1923).
[3] *Wied. Ann.*, **14**, 219 (1881).

B. The Equilibrium; Liquid-Liquid

The existence of two liquid phases in equilibrium implies a limited mutual solubility; where the solubility is unlimited, such a system cannot exist. A complete theory on which to forecast the extent of mutual solubility is not known; the topic will be treated in the third section of this chapter. It is possible however to arrange classes of substances, both liquid and solid, in an order representing in a rough way their solubility relations; the key to it is expressed in the phrase which has come down from the alchemists, *similia similibus solvuntur* (like is dissolved by like). Our selection of partially soluble liquids will therefore necessarily give us components which are quite dissimilar in composition, in general chemical properties, and particularly in such physical properties as degree of association and dielectric constant.

Upper Consolute Temperatures: Phenol and Water: When phenol and water are brought together at room temperature and in suitable proportions, two liquid phases result together with a vapor. This has become a classic instance of a two-liquid system. In studying it, we shall treat it as a condensed system, in view of the fact that changes of pressure (within reasonable limits) have but slight effect upon the equilibrium existing between the liquids; omitting therefore the vapor phase from reference and substituting a fixed pressure, we have a univariant system in which the relationship of temperature and composition will be studied. Alexejew,[1] to whom, with Guthrie, we owe the pioneer work on two-liquid systems, was the first to obtain a clear picture of the relations of these components; many others [2] have since added to the data on this system, and Rhodes and Markley [3] have recently completed the

TABLE XIX

The System: Phenol-Water[4]

Temperature	Wt. Per Cent Phenol in Phase L_1	Wt. Per Cent Phenol in Phase L_2
10°	7.5	
20	8.36	72.16
30	9.22	69.9
40	9.6	66.8
50	11.8	62.6
55	13.8	59.2
60	16.8	55.1
65	23.9	45.8
65.85	34.0	34.0

diagram, showing the relations of the liquids with the various solid hydrates and with ice. The two liquid phases formed at room temperature differ in

[1] *Wied. Ann.*, **28**, 305 (1886).

[2] Paterno and Ampola, *Gazz. chim. ital.*, **27**, I, 481 (1897); Rothmund, *Z. physik. Chem.*, **26**, 433 (1898); Schreinemakers, *Z. physik. Chem.*, **29**, 579 (1899); Scarpa, *J chim. phys.*, **2**, 447 (1904); Rozsa, *Z. Elektrochem.*, **17**, 935 (1911); Smits and Maarse, *Proc. Acad. Sci. Amsterdam*, **14**, 192 (1913).

[3] *J. Phys. Chem.*, **25**, 527 (1921).

[4] Hill and Malisoff, *J. Am. Chem. Soc.*, **48**, 918 (1926).

that one of them is water with a small proportion of phenol and the second is chiefly phenol with a small proportion of water; as the temperature rises, the proportion of phenol increases in the aqueous phase and the proportion of water increases in the phenol phase, until, at 68.4°, the two liquid phases have identical composition. Table XIX contains the data for the system.

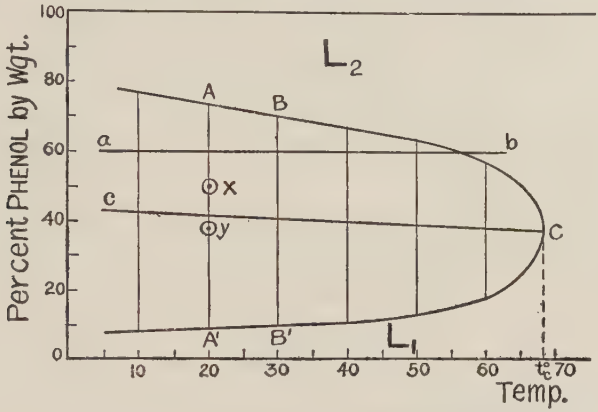


FIG. 11. *t.-c.* Diagram for the System Phenol-Water

The above data are plotted in Fig. 11. At any fixed temperature, such as 20°, the composition of the two liquid phases is necessarily fixed, the system being invariant, and the points are indicated by A and A'; the isothermal line joining them is spoken of as a *tie-line*, and the two solutions are called conjugate solutions.

If now, at this temperature, 50 per cent each of phenol and water are brought together, the composition of the complex will be represented by the point x; the complex will form two liquids of the compositions A and A'. The relative quantities of these phases formed may be calculated geometrically from the diagram; the weight of phase A formed will be the fraction $\frac{xA'}{xA' + xA}$ of the total, and that of A' will be $\frac{xA}{xA' + xA}$ so that the ratio of the weights of A to A' will be that of the lines xA' to xA; the weight of each is inversely proportional to the displacement of its composition from the composition of the total complex.

The effect of rising temperature upon this system is to increase the mutual solubility: the curve $A'B'C$ shows an increase in the concentration of phenol and the curve ABC an increase in that of water. At the point C, the curves merge into each other without discontinuity, and we have a critical state in the sense in which critical states have been defined above. What have been conjugate solutions at lower temperatures have now become a single solution; the temperature at which this phenomenon occurs is called the *consolute temperature*, or *critical solution temperature* (t_c). At higher temperatures, water and phenol are mutually soluble in all proportions, and the system can consist of but one liquid phase; below the consolute temperature, the mutual solubility is limited. No solution therefore can exist having composition indicated

by points within the area A–B–C–B'–A', but such compositions can lead only to two conjugate solutions of composition lying upon the curves at the intersections with the isothermal tie-lines.

The phenomena occurring at the consolute point are worth considering. Assume a complex y of the critical composition (34 per cent phenol) to be prepared at room temperature; it will yield two liquid phases of not very widely different weights. If the temperature is slowly raised, the quantities of the two phrases will vary slightly but not to any large extent, as can be seen from the diagram. If this system be stirred briskly, it will assume the characteristic milky appearance of an emulsion, always settling, however, into two clear phases. When the temperature 65.85° is reached, the turbidity vanishes sharply, so that the liquid is quite transparent; the passage from opacity to transparency is so definite that the temperature can be noted to 0.1°, and sometimes to 0.01°. If now the transparent liquid at a higher temperature is allowed to cool, the operations are reversed, and the turbid emulsion appears again at the consolute temperature.

If instead of a 36.1 per cent phenol-water complex, some other is taken and warmed, a series of changes occurs which has a superficial likeness to what has just been described, but must be sharply differentiated from the true critical changes. Assume a complex containing 60 per cent phenol to be warmed from 10° to 70°; the process can be followed by drawing a line of equal concentrations, ab, called an *isopleth*. At 10° the system will consist of about 4/5 of the phenol-rich phase lying at the bottom of the vessel used and 1/5 of supernatant aqueous layer, as can be calculated from the intercept of ab with the 10° isotherm. As the temperature is raised to 20°, 30°, etc., the quantity of the upper layer will diminish noticeably; if the system is stirred, it will be turbid, but will always settle into two transparent layers. After each rise of temperature, stirring and subsidence, the line of separation between the phases will be found nearer the upper surface; at 55°, the liquid will no longer show turbidity and the line of separation has reached the surface. We have passed from a two-liquid system to a one-liquid system; but we have *not* passed through a critical state. What has occurred has been merely the disappearance of a phase; what is required for a critical state is that two phases should become identical. It is only with the critical composition (in this system 34 per cent of phenol) that a critical state can be reached; with all other compositions, one phase increases at the expense of the other until the second has disappeared. In experimental practice, the distinction is not hard to observe; if the critical composition has been taken, the two phases will be *equal* in weight and volume just below the temperature at which they appear and disappear, as will be seen by marking a point just inside C and drawing a perpendicular (an isotherm) through it. On the other hand, for any other composition the two phases will be of unequal amount at a temperature just below that at which they appear; the new phase will appear as a mere drop or two at the top or the bottom of the container.

Systems like the one discussed above are said to possess an upper consolute temperature. A few generalizations for systems of this type may be made. The curve which represents the boundary of the two-liquid area, or the curve of conjugate solutions, is a continuous curve; its tangent at the consolute temperature is perpendicular to the temperature axis. The curve bears a resemblance to a parabola, but a generalized equation that should fit all cases has not been found. In general, the curve shows the largest changes in composition within a comparatively few degrees below the consolute temperature; in the case studied, the two liquids depart from each other by 22 per cent within the temperature range 65.85° to 65°. It has been found that a rough approximation to a "law of the straight diameter" [1] exists; that is, that a line con-

[1] Rothmund, *Z. physik. Chem.*, **26**, 433 (1898).

necting the middle points on the tie-lines, *A–A'*, *B–B'*, etc., is a nearly straight line as shown by *Cc* in Fig. 11. This relationship suggests at once the law of Cailletet and Mathias [1] for the densities of a liquid and its vapor approaching the critical state, and strengthens the analogy between the critical phenomena here discussed and those occurring in a liquid-vapor system. The statement is only an approximation, however; if the composition is expressed in molar fractions instead of per cent by weight, the curvature of the diameter becomes pronounced.[2] There is also to be noted, in systems showing consolute temperatures, a most interesting phenomenon in the area immediately above and around the critical point: the liquid, though plainly transparent, has a bluish haze, spoken of as the critical opalescence, which has occasioned much interest.[3] Although an optical condition of this sort might at first be thought to indicate heterogeneity, Smoluchowski [4] has shown that the optical effect is due to the scattering of light not by individual particles but by local variations of density arising from very slight inequalities in distribution. This critical opalescence, far from interfering with the experimental determination of the consolute point, has been found to be most helpful in indicating a close approach to the critical region.

The use of the terms solvent and solute in the case of two-liquid phases will be seen to be both inept and useless; no fundamental distinction between the function of the phenol and that of the water is known to exist, and certainly we cannot rightly regard one component as active and the other passive, as the words imply. Where we have in equilibrium two phases, of which one is of fixed composition and one of varying composition, as in the case of solid sodium chloride and its aqueous solution, it is a convenient usage to call the phase of fixed composition the solute and the component occurring only in the solution the solvent. If we have such a system as $Na_2SO_4.10H_2O$ and its aqueous solution, it is not easy to tell why we often speak of Na_2SO_4 as the solute; certainly no general definitions of the terms are possible.

The number of two-liquid systems showing an upper consolute temperature is considerable; a few of these will be given later in Table XXII.

Lower Consolute Temperature: Tri-ethyl Amine and Water: In a certain number of cases, the solubility curves for two-liquid phases approach each other with diminishing temperature, and meet at a lower consolute temperature which is analogous to the upper consolute temperature discussed previously. Tri-ethyl amine and water were found by Rothmund [5] to show this behavior. The data for this system follow.

[1] *Compt. rend.*, **102**, 1202 (1886).

[2] Menschutkin, *J. Russ. phys. chem. Ges.*, **44**, 1137 (1912); Aten, Roozeboom's Die heterogenen Gleichgewichte, 2, II, p. 61 (1918).

[3] Ostwald, *Lehrbuch*, II, 2, p. 683 (1902); Rothmund, *Z. physik. Chem.*, **26**, 433 (1898); Guthrie, *Phil. Mag.*, (5) **18**, 504 (1884); Friedländer, *Z. physik. Chem.*, **38**, 385 (1901); Timmermans, *ibid.*, **58**, 129 (1907); Konowalow, *Ann. Physik.*, **10**, 360 (1903).

[4] Smoluchowski, *Ann. Physik*, **25**, 205 (1908).

[5] *Z. physik. Chem.*, **26**, 433 (1898).

TABLE XX

THE SYSTEM: TRI-ETHYLAMINE-WATER

Temperature	Wt. Per Cent Amine in Phase L_1	Wt. Per Cent Amine in Phase L_2
70°	1.6	—
50	2.9	—
30	5.6	96
25	7.3	95.5
20	15.5	73
18.5	about 30	about 30

Fig. 12 is the plot of these figures. It will be noted that the curve is quite extraordinary; the mutual solubilities are very small at all temperatures above 25°, but increase enormously from 25° to 18.5°. The curve is, finally, nearly perpendicular to the temperature axis as a result, while it was not difficult to obtain the consolute temperature with considerable accuracy, the corresponding composition is not at all accurately known. The observation of the critical opalescence, which is most pronounced when closest to the consolute point, indicates that the composition is not far from 30 per cent.

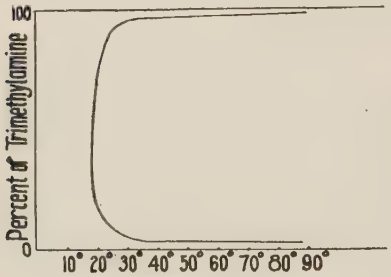


FIG. 12. *t.-c.* Diagram for the System, Triethylamine-Water

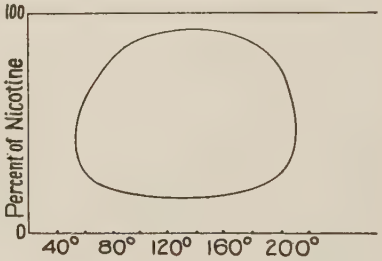


FIG. 13. *t.-c.* Diagram for the System, Nicotine-Water

Most of the other substances showing lower consolute temperatures are amines, and therefore not easy to bring to a high state of purity; since the presence of a third component has been shown [1] frequently to have a very pronounced effect upon the consolute temperature, it is possible that the figures for this class are less accurately known than those of the previous class. In none of these latter instances is the law of the straight diameter even approximately applicable.

Completely Closed Solubility Curves: Nicotine and Water: With a knowledge of solubility curves closed at higher temperatures and others closed at lower temperatures, it is natural to look for cases where the curves are closed at both temperatures, i.e., systems with both upper and lower consolute temperatures. Hudson [2] was the first to discover such an example in nicotine and

[1] Timmermans, *Z. physik. Chem.*, **58**, 187 (1907); Friedländer, *Z. physik. Chem.*, **38**, 385 (1901); Dolgolenko, *Z. physik. Chem.*, **62**, 499 (1908); Crismer, *Bull. Acad. Sci.*, **30**, 97 (1895).

[2] *Z. physik. Chem.*, **47**, 114 (1903).

water; Tsakalotos [1] confirmed the data of Hudson within a few per cent. In Table XXI are given, not the two conjugate compositions for a fixed temperature, but the two temperatures corresponding to a fixed composition; this follows from the isoplethal method of experimentation used by Hudson which will be described later. Either method will give a complete set of points by which the entire closed curve may be plotted. Fig. 13 represents the curve.

TABLE XXI

THE SYSTEM: NICOTINE-WATER

Per Cent Nicotine by Weight	Lower Temperature	Upper Temperature
6.8	94°	95°
7.8	89	155
10.0	75	—
14.8	65	200
32.2	61	210
49.0	64	205
66.8	72	190
80.2	87	170
82.0	129	130

Tsakalotos finds that the composition for both critical points is the same, namely, 34 per cent of nicotine; the lower temperature is 60.8°, the higher 208°. Between these temperatures two conjugate liquids may be obtained; beyond them, or, in general, outside of the closed curve, only one is possible, and the liquids are completely soluble.

A completely closed curve, such as that of Fig. 13, must have points of maximum and of minimum solubility. At these points the tangents to the curve are parallel to the temperature axis. Applying van't Hoff's law of mobile equilibrium, from the fact that at these points the solubility does not vary with the temperature, it follows that the heat of solution is zero. The heat of solution concerned is not that of the pure components, but the heat change upon removing from the saturated solution a quantity of the saturating solution, which is represented at the other end of the tie line at the temperature of maximum or minimum solubility. Beginning at each such point the curve rises with rising temperature in one direction and falls with rising temperature in the other; the branch which shows a rise with the temperature, that is, possesses a positive coefficient of solubility, represents solutions in which the heat of solution is negative, and vice versa for the other branch.

Table XXII gives the critical data for some of the types of systems discussed above.[2]

[1] *Bull. soc. chem.*, **5**, 397 (1909).

[2] For a fairly complete list of known cases, see Roozeboom's Die heterogenen Gleichgewichte, 2, II (Aten), pp. 70, 73, 74, 76, 78, 81. To these add Keyes and Hildebrand, *J. Am. Chem. Soc.*, **39**, 2126 (1917); McKelvey and Simpson, *ibid.*, **44**, 105 (1922); Kraus et al., *ibid.*, **44**, 1249 and 1949 (1922).

TABLE XXII

CRITICAL DATA FOR TWO-LIQUID SYSTEMS

Systems Having Upper Consolute Temperatures			Systems Having Lower Consolute Temperatures		
Substances	Wt. Per Cent of First-named Component	Consolute Temp.	Substances	Wt. Per Cent of First-named Component	Consolute Temp.
Methyl alcohol-hexane [1]	30.1	42.6°	Carbon dioxide-o-nitrophenol [7]	72	23°
Succinic nitrile-water [2]	51	55°	Di-ethyl amine-water [8]	13	143°
Carbon disulfide-methyl alcohol [3]	85	35.7°	β-Collidine-water	4	6°
Aniline-hexane [4]	52	59.6°	1-Methyl piperidine-water [9]	5	48°
Benzene-sulfur [5]	35	163°			
Aluminum bromide-[6] sodium bromide	92	232°			

Systems Having Both Upper and Lower Consolute Temperatures

Substances	Wt. Per Cent of First-named Component	Lower Consolute Temp.	Wt. Per Cent of First-named Component	Upper Consolute Temp.
Methyl ethyl ketone-water [10]	31	− 6°	20	133°
β-Picoline-water [11]	7	49°	9	153°
$\alpha\alpha$-Lutidine-water [11]	7	45°	10	164°
3-Methyl piperidine-water [11]	4	56°	8	236°
4-Methyl piperidine-water [11]	5	85°	8.5	189°
2-Methyl piperidine-water [12]	4	79°	6	227°

[1] Rothmund, *Z. physik. Chem.*, **26**, 433 (1898).
[2] Schreinemakers, *Z. physik. Chem.*, **23**, 439 (1897).
[3] McKelvey and Simpson, *J. Am. Chem. Soc.*, **44**, 105 (1922).
[4] Keyes and Hildebrand, *J. Am. Chem. Soc.*, **39**, 2120 (1917).
[5] Alexejew, *Wied. Ann.*, **28**, 305 (1886).
[6] Kendall, *J. Am. Chem. Soc.*, **45**, 968 (1923).
[7] Büchner, *Z. physik. Chem.*, **30**, 665 (1906).
[8] Lattey, *Phil. Mag.*, **10**, 397 (1905).
[9] Flaschner, *Z. physik. Chem.*, **62**, 493 (1908).
[10] Timmermans, Roozeboom's Die heterogenen Gleichgewichte, 3, II, p. 76.
[11] Flaschner, *J. Chem. Soc.*, **95**, 668 (1909).
[12] Flaschner and McEwen, *ibid.*, **93**, 1000 (1908).

Conjugate Liquids Without Consolute Points: There is a very large number of conjugate liquid pairs which possess neither an upper nor a lower consolute temperature. This is the case with ether and water and with chloroform and water; it is probably the case with any pair whose mutual solubility is very low. As temperatures are lowered in such cases, a point is reached at which a solid phase appears; where water is one of the components, this occurs not far below 0°, since the concentration of the second component in the water and its effect upon the freezing point are small. There are, therefore, four phases present ($S - L_1 - L_2 - V$) and the system is invariant; if subjected to a cooling environment, ice continues to form until the aqueous layer has completely disappeared, and the system of conjugate solutions cannot exist at any lower temperature. The exact relations will be shown in a later paragraph. If, on the other hand, the temperature be raised, a point will finally be reached at which one of the liquids, namely, that one rich in the more volatile component, is at its critical state; the vapor above it has reached not only the same relative composition as the liquid phase, but also the same density, and one of the two-component liquid phases disappears in the same fashion as at the critical temperature for a one-component system. Ether and water are known to behave thus.

At $-3.83°$ the solid phase appears,[1] and below this temperature only the ethereal liquid phase exists. At this temperature the ethereal phase contains only about 1 per cent of water, and the increase with temperature rise is very small; the aqueous phase contains 12.7 per cent ether, but has a negative solubility coefficient, so that the ether content has fallen to 5.34 per cent at 30°; at 82°, it has fallen to 2.7 per cent.[2] Kuenen[3] and Robson have found that at 201° the ethereal phase, which contains about 2 per cent of water, reaches its critical state, above which only the water phase can exist as a liquid. Generalizing from the behavior of this system, we may say that where a system of conjugate liquids does not show an upper nor a lower consolute temperature, it terminates at low temperatures with the disappearance of the phase rich in the component of higher melting point, and at higher temperatures through the disappearance of the phase rich in the more volatile component at a critical point for the system liquid-vapor.

Space does not permit a study of two-liquid systems in which the pressure is treated as a variable. Suffice it to say that, in accordance with Le Chatelier's theorem, pressure must increase mutual solubility where solution is accompanied by a diminution in volume, and decrease solubility in the infrequent cases where an increase in volume occurs. The effects upon the solubility are usually of small order. In a number of cases high pressures have, however, altered the location of consolute points considerably.

Experimental Methods: The most commonly used method for determining the mutual solubility of two liquids is that devised by Alexejew[4]; it consists in introducing known weights of the two liquids into a small glass tube, which is then sealed and rocked in a bath in which the temperature rises slowly; the

[1] Hill, *J. Am. Chem. Soc.*, **45**, 1143 (1923); this article contains a bibliography of the system.

[2] Klobbie, *Z. physik. Chem.*, **24**, 615 (1897).

[3] *Z. physik. Chem.*, **28**, 342 (1899).

[4] *Wied. Ann.*, **28**, 305 (1886).

temperature at which the two-phase emulsion becomes clear gives a point on the curve, which may be confirmed by cooling the clear liquid until it becomes turbid. A series of such points will give the complete outline of the curve, as shown above in the data for nicotine and water. Regarding the system as a condensed system, the effect of the pressure within the tube may be neglected. This extremely useful method of experimentation, called by Rothmund [1] a synthetic method, may be more properly classified as *plethostatic*,[2] since it consists in using a system of fixed composition and determining the temperature at which conjugate liquids appear. *Thermostatic* methods are those in which the temperature of a system is fixed, and the composition of the two liquids subsequently determined after sufficient agitation has brought them to equilibrium; this can occasionally be done by direct analysis, though usually liquids do not lend themselves to easy analysis. A thermostatic method, dependent upon volumetric measurements,[3] consists in weighing the two components into each of two vessels in differing amounts, and determining the volumes produced after equilibrium has been obtained at a fixed temperature; graduated cylinders may be used in place of more accurate apparatus.

Let m and m' represent the weights of the first component used in the two experiments; let x represent its concentration in grams per cubic centimeter at equilibrium in the upper phase in both experiments, since by the phase rule the concentration at saturation cannot vary; and, similarly, let y represent its concentration in the lower phase in both experiments. If, now, the measured volumes of the upper phase are a and a', and the volumes of the lower phase b and b', it follows that $ax + by = m$, and $a'x + b'y = m'$.

Solving the equations for x and y will give the concentration of the first component in each phase, expressed in g. per cc. of solution. If the equations are again solved, substituting in place of m and m' the weights n and n' of the second component, its concentration in each phase becomes likewise known in the same units. By adding together the weight of each component present in 1 cc. of a given phase, the weight per cubic centimeter, or density, is obtained, and the percentage composition by weight thus follows. A single pair of experiments will, therefore, give the solubility in unit volume and in unit weight. This procedure involves no assumptions as to changes of volume occurring.

In addition to plethostatic and thermostatic methods, *barostatic* methods are conceivable; none have been devised.

C. The Equilibrium: Solid-Liquid

In passing to systems of two components in which solid phases are considered, the relations differ markedly according as such phases consist of pure components, compounds, or solid solutions. The classification which will be used in the effort to give as complete a treatment as possible within short space is as follows:

I. The solid phases consist of pure components only.
   (*a*) Only one liquid phase appears; i.e., the fused components have unlimited solubility.
   (*b*) Two liquid phases appear; i.e., the fused components have limited solubility.

[1] *Z. physik. Chem.*, **26**, 443 (1898).
[2] Hill, *J. Am. Chem. Soc.*, **45**, 1143 (1923).

II. The solid phases consist of compounds.
  (*a*) The solids show transition points, but no melting points.
  (*b*) The solids show melting points, called congruent melting points.
III. The solid phases consist of solid solutions.
  (*a*) Only one solid solution forms; i.e., the solids show complete mutual solubility.
  (*b*) Two solid solutions form; i.e., the solids show limited mutual solubility.

Ia. Pure Components as Solid Phases, with a Single Liquid: We shall develop a diagram of an entirely general nature for this case and afterward show that it indicates, at least qualitatively, relations which are met with in some of our commonest laboratory experimentation, such as the determination of melting points and of the solubility of solids in liquids, as well as in important

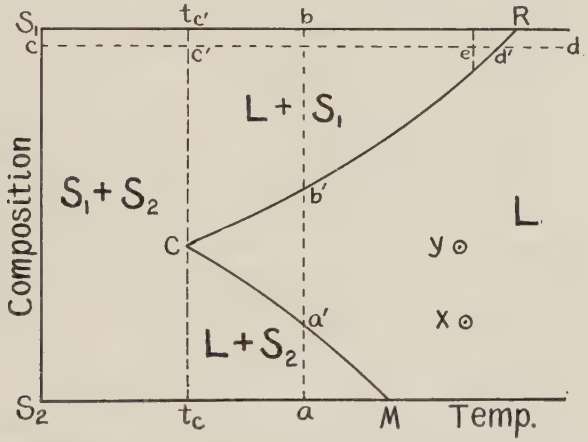


FIG. 14. The System $S_1 - S_2$. The Solid Phases are Pure Components, with one Liquid Phase Present

commercial operations, such as the manufacture of metallic alloys. Treating our systems as prepared under the pressure of their own vapor, or under atmospheric pressure, and omitting the vapor phase from consideration, we may use Fig. 14 to represent the temperature-composition relations of the system $S_1 - S_2$. Here the point R represents the freezing point of pure S_1; as increasing quantities of S_2 are added, the freezing point falls along the curve RC, which therefore represents the equilibrium of S with the liquid phase. In like manner M is the freezing point of S_2 and MC its freezing-point curve. Since in all cases the freezing point of a component which exists in the solid phase in pure condition is lowered by the presence of a second component in its solution, the two curves must take the general direction here indicated and must intersect at some point C, which will be discussed later; our freezing-point diagram therefore must show discontinuity, and the two branches to the

curve represent respectively S_1 as solid phase in equilibrium with liquid and S_2 as solid phase in equilibrium with liquid. The two curves have been spoken of as freezing-point curves; they are also correctly named solubility curves, since they represent the concentration of the solutions saturated with a given phase at a given temperature, which is a definition of solubility. It is worth emphasizing that there is no distinction of any sort between a freezing-point curve and a solubility curve since each represents the temperatures and compositions for the equilibrium between solid and liquid. Most of our solubility data in the literature represent simply sections of the general curve CR or CM. It is also worth noting that in a two-component system of this type there is qualitative equivalence in the functions of the two components; that is, one is the solid phase through a part of the range of composition, and the other through the remainder.

The diagram for a solubility curve such as CR is here given in its simplest form; it will frequently show wide variations from the simple form indicated here, the only unvarying condition being that it necessarily begins at the point of intersection C and ends at the melting point R. It may, for example, show a discontinuity in direction at some intermediate point; as previously stated, this is evidence of a change of phase and must represent (since compound formation is here left out of discussion) that the solid phase has a transition point from one polymorphic form to another. The curve for the equilibrium of silver nitrate (solid phase) and water shows such a transition point at 160°; that for ammonium nitrate (solid phase) and water shows breaks at 32°, 82.7°, and 125.6°. Moreover, the curve sometimes fails in part of its course to maintain its slope toward the axis of the solid component with temperature rise. A slope in this direction means an increase in solubility with rising temperature; but numerous instances exist in which the solubility decreases with rising temperature, well-known cases being calcium chromate in water and calcium citrate in water. Maximum and minimum points in the solubility curve are also by no means uncommon. All of these directions and changes of direction can be derived from van't Hoff's law whenever the thermal data are available; the solubility curve is ascending at a given point when the heat of solution in the saturated solution is negative at that point, is descending when the heat of solution is positive at that point, and is neither ascending nor descending (which is the condition at a point of maximum or minimum solubility) when the heat of solution is zero. In applying this law, however, it is necessary to remember that the heat of solution which governs the direction of the equilibrium by its sign is the heat of solution at *saturation*, i.e., the heat developed by the last increment entering the solution. Van't Hoff's law has to do with a displacement of an equilibrium by thermal means; it is clear that what may happen in a system not yet in equilibrium (i.e., not yet saturated) is altogether irrelevant. A recollection of this method of applying the law is essential if one is to avoid error. For example, it is common knowledge that when water is poured upon solid potassium hydroxide, much heat is evolved; if one deduced therefrom that the solubility of the compound decreased with

the temperature, the error would be flagrant. The initial heat of solution is positive; it may be that the total heat of solution is positive; but the final heat of solution, representing the dissolving of the last increment entering the solution at the saturation point, is negative, and hence a rise of temperature will result in the dissolving of another increment.

Returning to Fig. 14, a solubility curve such as *C–R* represents saturation or equilibrium conditions; it separates two regions in which solutions may occur, stable or metastable. The area to the right of the curve *C–R* is the region of unsaturated solutions; that to the left is the region of metastable supersaturated solutions. A phase-rule distinction between these three types of solutions is not only simple, but is the only logical one. A saturated solution is one in equilibrium with the solid phase, and is therefore unaffected by addition of more solid phase; an unsaturated solution is one which will dissolve more solid phase if it be added, and a supersaturated solution is one which, being metastable, will precipitate solid phase from its own composition and fall to the point of saturation if a nucleus of the solid phase be added. All concepts of degrees of saturation must always refer to a particular solid or saturating phase (S_1 in the case of the curve *C–R*), since a solution in equilibrium with one phase is quite capable of entering into new relations of saturation with respect to some second phase.

The intersection of the two-solubility curves (*C*), called the *eutectic point*, is the most interesting point of the diagram. Since the curve *RC* represents solutions saturated with S_1, and *MC* solutions saturated with S_2, the intersection must represent a solution saturated with both solids. The system represented by this point consists of two solid phases, solution and vapor, and is called a quadruple point; by the phase-rule equation, it is an invariant point. A solution to be in equilibrium with both solids can have therefore only the eutectic composition *C* and can exist in stable equilibrium only at the eutectic temperature, t_c. Rise of temperature above t_c results in the disappearance of one or both solid phases, and fall of temperature in the disappearance of the liquid. The eutectic point may be defined in terms of these phenomena; it is an invariant temperature at which the phase reaction of the system, upon removal of heat without change of temperature, results in the disappearance of the liquid phase.

In a system including a eutectic we have a simple and widely used means of securing a constant temperature. If two solids, properly chosen as to their solubility relations, are brought together in the eutectic proportion or any proportion approximating the same, they will begin the process of dissolving which, being endothermal in all common cases for both solids, reduces the temperature to the eutectic temperature. If, now, the system is well enough insulated so that heat can reach it from without only at a moderate rate, and is well stirred so that solution of the solids can occur quickly and temperature inequalities be eliminated, it will remain constant at the eutectic temperature until one of the solids has dissolved completely. With proper apparatus, extremely constant temperatures result; but, as pointed out in our introduction, it does not follow that the equilibrium will be reached at all if the apparatus is unsuited. Thus, the eutectic temperature for sodium chloride and water is $-22.4°$, and a coarse mixture of the two solids, ice and salt, gives a reasonably

effective freezing mixture for the household ice-cream freezer; but it is doubtful if this mixture, poorly insulated from the outside and warmed from the inside, practically free from stirring and with the salt and ice poorly mixed, ever gets within many degrees of $-22°$; that is, no equilibrium is reached. But, if snow and fine salt be put in a Dewar flask and well stirred, a perfectly constant temperature may be maintained for hours; equilibrium is really attained. Examples of other eutectic temperatures and compositions will be given later in Table XXVIII, together with eutectics of other classes.

The existence of eutectics for systems of salts and water was first observed by Guthrie.[1] At first, in the absence of knowledge of the phase rule, incorrect interpretations were made. The solid separating out was thought to be a compound, and was called a cryohydrate, the point being named the cryohydric point. The view that the solid was a compound was based upon its constant composition; for, it will be seen (Fig. 14) that if the solution C deposits solid by abstraction of heat and at the same time itself remains unchanged in composition, as the phase rule requires for an invariant point, the solid precipitated must be of the same composition as the liquid and will therefore also have an unvarying composition; reversing the process and warming this solid material, it will melt at a constant temperature, which is likewise the behavior of a pure compound. The fact that the solid is not a compound, but a mixture of solid phases, was shown by Pfaundler [2] and Ofer [3] who showed the identity of the physical properties of this material with those of a mixture; heterogeneity can sometimes be detected by careful direct examination, and always by means of microscopical examination. Constancy of composition and constancy of melting point alone, it will be seen, cannot establish a chemical compound; the application of the phase rule (here nothing more intricate is involved than the intersection of two lines) is, however, adequate to settle the question. It will later be shown that the evidence of the phase rule may be not only negative as to compound formation, as in this instance, but may also be positive.

The general diagram of Fig. 14 may be used to illustrate the effect of isothermal and isoplethal changes. Assume that pure component S_2 be taken at some temperature, a, below the melting points of both compounds and that S_1 be added to it continuously at constant temperatures; the isotherm ab will indicate, by its intersections, all the changes which occur. Addition of solid S_1 will produce at once a small amount of solution of the composition a', in equilibrium with S_2, as indicated by $a'a$, serving as a tie-line between the liquid and solid, which bear a conjugate relation to each other. Addition of more S_1 will increase the mass of the solution a' without altering its composition, since it is a saturated solution at that temperature, but the mass of solid S_2 decreases by dissolving; finally all S_2 has dissolved, and the composition falls on $a'b'$ above a'. The solution is now unsaturated with respect to either solid, and grows richer in S_1 until the composition b' is reached, which is that of a

[1] *Phil. Mag.*, (4) **49**, 1, 206, 266 (1875).
[2] *Ber.*, **20**, 2223 (1877).
[3] *Sitz.-Ber. Wien. Akad.*, **81**, II, 1058 (1880).

solution saturated with S_1; from this point onward the composition of the liquid remains fixed while its relative quantity diminishes until the point b, representing pure solid S_1, is reached.

For an isoplethal study, we will assume a complex of S_1 containing a very small amount of S_2, as represented by c; this will serve not only to show all the phase changes possible, but will illustrate the very practical experiment of taking the melting point of a slightly impure solid. At c the complex consists of a mixture of two solids, S_2 being present only in traces; as the temperature rises along the isopleth c–d, no change occurs until the eutectic temperature, t_e, is reached. Here, liquid phase of the composition C is formed, and solid S_2 disappears in the formation of the solution; the relative amounts of solid S_1 and of solution are represented by the lengths $c'C$ and $c't_e$. Now, if our total composition were nearer that of C, the amount of the solution would be sufficient to be visible, and there would be a halt in the rise of temperature of the system while the endothermal formation of this solution was occurring; but, with the composition which we have purposely chosen, the amount of the liquid is so small that it is not visible, any more than would be a drop of water poured upon a bucket of sand, and there is no detectible halt in the temperature rise. As we now pass along $c'd'$ toward d', the length $t_{e'}$–c' representing the relative mass of solution remains constant, while the length representing the mass of solid S_1 is constantly decreasing, which means that in reality we are obtaining more liquid phase and losing solid phase. At some point, e, the amount of liquid becomes large enough to be seen, and the total mass "softens"; from then onward it becomes softer and softer, until at d' it clarifies completely with the disappearance of solid. To speak in the inexact terms of the experiment, the solid did not melt sharply, but melted between the temperatures e and d'. It will be seen that the length of this temperature interval decreases as the isopleth is raised toward the axis S_1, so that the "sharpness" of the melting point is a criterion of the purity of S_1. Only in the complete absence of a second component does the substance possess a true melting point, R.

Systems of two components which are represented diagrammatically by Fig. 14 are very numerous. They include many pairs of organic compounds and of inorganic compounds; salts with water fall into this class in numerous instances, and the solubility curve of a salt as given in the various solubility tables is usually a section, more or less complete, of one of the curves of the diagram; metallic alloys occasionally fall into this class. The term alloy is so broadly used that it is not easily defined; most simply phrased, an alloy is a substance containing two or more components which are metals. In practice, however, we do not hesitate to apply the term to iron-carbon alloys, in which only one of the components is a metal. In Table XXIII are given three typical cases of systems which may be represented by Fig. 14.

In the case of alloys, the conditions at the eutectic are of importance, not only as determining the lowest melting point for the metallic pair but also as affecting the structure and physical properties of the solid alloy. If some composition other than the eutectic composition be taken and the molten metallic solution cooled, upon reaching the freezing-point curve RC or MC in Fig. 14 (dependent on whether S_1 or S_2 is in excess), crystals of the one component begin to form throughout the liquid mass. When the temperature has dropped to the eutectic temperature, t_e, it will there remain constant and crystals of both S_1 and S_2 will form in the eutectic ratio and continue to form until the mass is entirely solid. This crystallization of the two solids in a continuously uniform ratio fills in the interstices between the crystals previously formed with

TABLE XXIII

SOLUBILITY CURVES WITH EUTECTICS

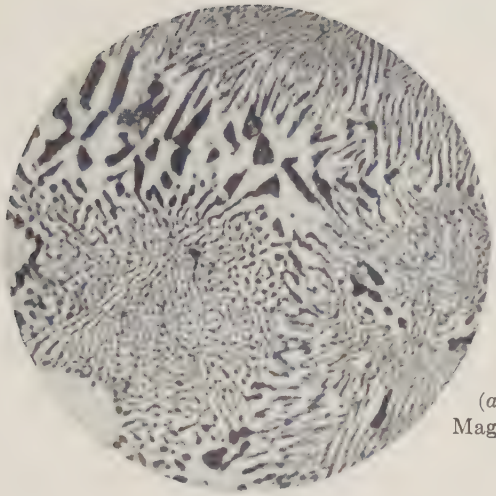
Point	Cyclohexane: Benzene [1]		Silver Nitrate: Water [2]		Lead: Silver [3]	
	Temp.	Per Cent Cyclohexane	Temp.	Per Cent Silver Nitrate	Temp.	Per Cent Silver
M	+ 5°	0	0°	0	327°	0
	− 5.2	17.04				
	− 11.3	28.26				
	− 26.9	52.88				
	− 36.2	65.05				
C	− (44)	(75)	− 7	46.2	303.3	5
	− 37.1	78.55	+ 5	56.3	460	10
	− 31.2	84.56	20	67.8	535	20
	− 16.5	88.34	40.5	76.8	648	50
	− 6.7	93.42	135	92.8	875	85
R	+ 6.2	100	208	100	961.5	100

[1] Mascarelli and Pestalozzi, *Gazz. chim. ital.*, **38**, 38 (1908).
[2] Etard, *Ann. chim. phys.*, (7) **2**, 524 (1894).
[3] Petrenko, *Z. anorg. Chem.*, **53**, 200 (1907).

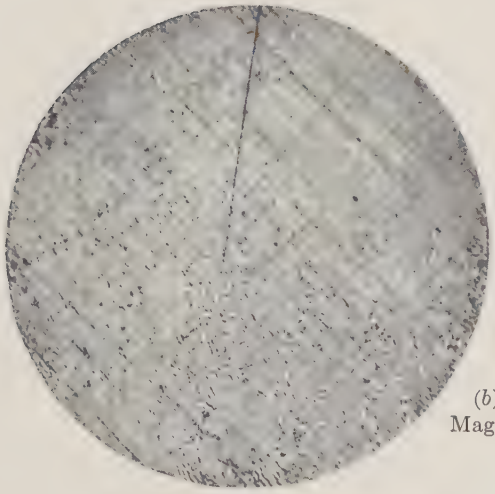
a conglomerate which, though truly a mixture, is remarkably uniform in character. By the methods of metallography, such metallic surfaces can be examined under the microscope; under high magnification the eutectic mixture shows its heterogeneity, as in Fig. 15*a*, but its approximation to homogeneity as shown in Fig. 15*b* is such that in metallographic work it is looked upon as a "structural element" as if it were a single phase.

Ib. Pure Components as Solid Phases, with Two Liquid Phases Occurring: It has previously been pointed out that if a system of two conjugate liquids with an upper consolute temperature be cooled, and if it be the fact that no lower consolute point exists, a solid phase will eventually appear. There will then be present four phases ($S - L_1 - L_2 - V$) and the system is invariant. Such a system must show in its graph a two-liquid area in connection with a solubility curve such as was discussed in the preceding examples; Fig. 16 is a type figure drawn to represent such relations, in which the points A and B represent the composition of the two conjugate liquids which are in equilibrium with the solid phase S_1 at the temperature t. It will be seen that such a system contains the two-liquid curve shown earlier in Fig. 11 and the two solubility curves shown in Fig. 14, the difference being in the apparent break in the solubility curve CB–AR (Fig. 16) at its points of contact with the two-liquid curve. The only new considerations that enter are, therefore, limited to this point in the diagram.

The temperature t at which these four phases are in equilibrium gives us an added example of a quadruple point. We have previously discussed the eutectic as such a point, the phases being $S_1 - S_2 - L - V$; the transition



(*a*)
Magnified 500 times



(*b*)
Magnified 150 times

Fig. 15

Ag-Cu Alloy, Slightly to the Cu Side of the Eutectic Point (73% Ag, 27% Cu)

Diagrams by courtesy of
Prof. D. P. Smith and Mr. J. L. Whitten

temperature of two polymorphic forms, mentioned previously but not discussed, is of the same class, with two solids, one liquid and vapor; our new example differs in having two coexisting liquids. No specific name has been given to this type of quadruple point, but it is nevertheless one of considerable interest. Its recognition gives us a phase-rule explanation of a common occurrence in organic practice, namely, the so-called "melting under water" of various compounds; this phenomenon occurs frequently at temperatures far below the true melting point of the pure compound. It will occur invariably in two-component systems of the type under discussion if one experiments with complexes of a composition intermediate between *A* and *B*, the two conjugate solutions; such a complex is represented by *x* in Fig. 16.

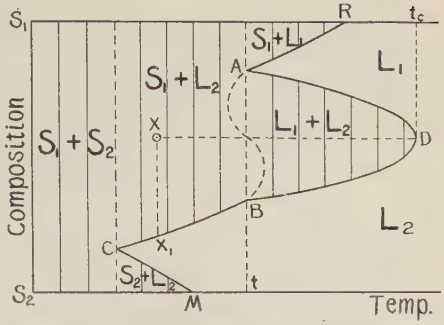


FIG. 16. The System $S_1 - S_2$. The Solid Phases are Pure Components with Two Liquid Phases Present

At the initial temperature of *x*, the system consists of the solid S_1 in equilibrium with its saturated solution *x'*, as can be read from the diagram; if the temperature be raised along the isopleth *xD*, the concentration of the solution rises along *CB*, finally reaching the composition *B*. At the quadruple point *t* the temperature rise will halt, and as the solid S_1 continues to dissolve, a new liquid phase begins to form, of the composition *A*. It will be seen that the new liquid is *not* simply a layer of molten S_1, but is a solution; the phenomenon is then not at all the melting of a solid into a liquid of identical composition, as happens with a pure one-component body, but is the formation of a second conjugate liquid. On continued application of heat, the solid S_1 will disappear completely, and only two liquids (with vapor) remain; the continuation of the isopleth to the point *D* has been discussed in connection with Fig. 11.

This phenomenon of "melting under water," or indeed under any other liquid, since it represents an invariant temperature, is a perfectly definite property for any compound, and might serve as a criterion of its purity, although in practice other properties are more convenient. A few examples of such quadruple points follow.

TABLE XXIV

THE QUADRUPLE POINT $S - L_1 - L_2 - V$

Substances	M.P. of Pure Component	Quadruple Temp.	Wt. Per Cent of First-named Component	
			L_1	L_2
Benzoic acid-water	121.4°	98°	71	7
Phenol-water	42.7	1.7	72	2.5
Succinic nitrile-water	53	18.5	92	10.2
Water-ether	0	− 3.8	99	87.3
Resorcin-benzene	110	95.5	68.5	15

At invariant temperatures such as appear at t and t_c in Fig. 16 there occur phase reactions; that is, the addition or subtraction of heat results in the passage of substances from one phase to another, without change of temperature, and in the ultimate appearance or disappearance of a phase. The course of such phase reactions can be easily followed from the diagram.

At the temperature t, omitting reference to the vapor phase, which will be present after the reaction as well as before, the compositions of the three phases which bear a conjugate relation, as shown by the tie-line t, are represented by S_1, A and B. Of these, A (one of the solutions) is intermediate in composition between S_1 and B; it follows geometrically that A can be formed from certain quantities of S_1 and B, but that it is impossible to form S_1 alone from any quantities of A and B, or B alone from any quantities of A and S_1. The phase of intermediate composition is formed always from those of the extreme composition, and the phase reaction which occurs upon adding or subtracting heat is

$$S_1 + L_2 \rightleftharpoons L_1,$$

where L_2 stands for the composition B and L_1 for the composition A.

It remains to decide which of these reversible changes occurs upon addition of heat and which upon subtraction. If thermal data are available, the conclusion could be reached by use of van't Hoff's law; but in the absence of such data, the diagram will give the answer. Inspection shows that areas in which L_1 is represented exist only at temperatures above t, while S_1 and L_2 exist both below and above that temperature; hence, the arrow pointing to the right represents the reaction resulting upon addition of heat and is endothermal. We may also deduce what univariant equilibria (two phases plus vapor) have their origin at this quadruple point. There will be as many as there are combinations of two out of the three phases, which are:

$S_1 + L_2$, at lower temperatures (curve BC),
$L_2 + L_1$, at higher temperature (curve BDA),
$L_1 + S_1$, at higher temperature (curve AR).

If now we apply the same reasoning to conditions at the other quadruple point, namely, the eutectic C, we obtain the following:

Phase reaction: $S_1 + S_2 \rightleftharpoons L_2 - X$ calories.

Univariant equilibria: $S_1 + S_2$, at lower temperatures,
$S_1 + L_2$, at higher temperatures (curve $CB - AR$, since L_1 and L_2 are equivalent when not conjugate),
$S_2 + L_2$, at higher temperatures (curve CM).

From the invariant points existing for the system, we have deduced all the univariant equilibria which exist (i.e., all the curves of Fig. 16). There remains for discussion only the question of the solubility curve for $S_1 + L$ between the points A and B. To this is ascribed an S form (shown in the

dotted lines), with a point of inflection, such as is drawn to represent the van der Waals equation for $p - v$ relations of a gas and liquid, and such as has previously been shown in Fig. 10. Of course, all parts of this are either metastable or unrealizable.

As a complete example of a system represented by Fig. 16, the data for succinic nitrile and water are given in Table XXV.

TABLE XXV

SUCCINIC NITRILE AND WATER[1]

Solubility Curves			Conjugate Liquids: Curve *BDA*			
Temp.	Mol. Per Cent Nitrile	Point	Temp.	L_2 Mol. Per Cent	L_1 Mol. Per Cent	Point
0°	0	*M*	18.5°	2.5	72	*B, A*
− 1.2	1.29	*C*	20	2.7	70.7	
0	1.36		39	—	56.4	
17	2.3		45	5.97	—	
18.5	2.5 and 72	*B, A*	53.5	10	30.7	
24	76.6		circa (55.5)	circa 20	20	*D*
29.3	81.2					
54.5	100	*R*				

[1] Schreinemakers, *Z. physik. Chem.*, **23**, 439 (1897).

As special cases falling into this class should be included systems in which the conjugate solutions are metastable, i.e., the curve *ADB* is wholly to the left of the solubility curve *CBAR*, as Alexejew found for salicylic acid and water,[2] and also the rare instances in which the conjugate solutions show a lower consolute temperature, in which case the conjugate curve is conjoined to a descending solubility curve; such a relation exists in the system: potassium iodide-sulphur dioxide.[3]

IIa. Compounds as Solid Phases, without Congruent Melting Points: Systems of this type introduce few considerations not already advanced. They are, however, extremely common; whenever any two components show a high degree of solubility, it is probable that there is more or less compound formation in the liquid phase, and frequently one or more of these compounds will form solid phases as well; the formation of solid hydrates of salts for example is of the commonest occurrence. The classical instance of a system of this type is given by sodium sulfate and water; studied first more than a century ago by Zis and by Gay-Lussac,[4] it has had its various solubility curves and transition points determined by a number of investigators, the work having been completed recently by Wuite[5] at the high temperatures leading up to the

[2] *Wied. Ann.*, **28**, 305 (1886).

[3] Walden and Centnerszwer, *Z. physik. Chem.*, **42**, 432 (1903).

[4] Zis, *Schwegg. Journ.*, **15**, 160 (1815). Gay-Lussac, *Ann. chim. phys.*, **11**, 296 (1819).

[5] *Z. physik. Chem.*, **86**, 349 (1914).

critical temperature of the solution. The composition-temperature diagram is shown schematically in Fig. 17. The curve AB is the freezing-point curve for ice, which ends at the eutectic B ($-$ 1.2°); here the other solid phase is the decahydrate, $Na_2SO_4.10H_2O$, which is an additive compound formed of the two components. The solubility curve for the decahydrate rises with the temperature up to 32.4°, which is its transition temperature (F.) to the an-

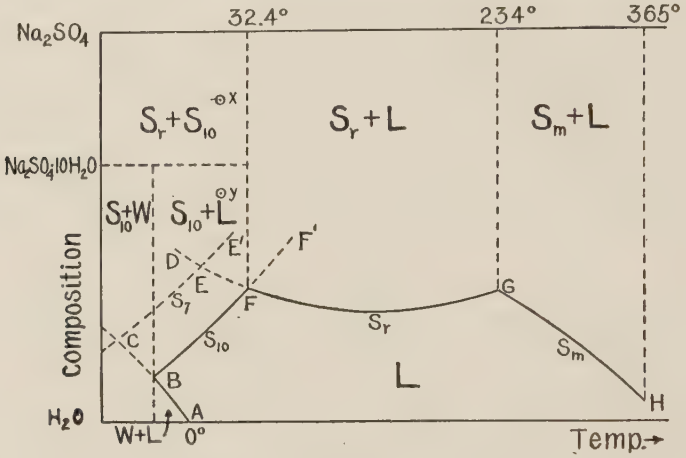


Fig. 17. *t.-c.* Diagram for the System, Sodium Sulfate-Water

hydrous form and the distinctive point of this diagram. The curve for the anhydrous sulfate shows a solubility diminishing with rise of temperature up to about 125° where it reaches a minimum value, afterward rising until the temperature is 234°. Here (point G) occurs a transition from the common crystalline form, which is rhombic, to a polymorphic monoclinic form which has a diminishing solubility up to 365°, which is the critical temperature of the solution; the concentration of the salt in the liquid phase is here very low and the critical temperature is practically that of pure water. The four solid phases occurring in equilibrium with solution along this curve are represented by W (ice), S_{10} (decahydrate), S_r (rhombic anhydrous salt) and S_m (monoclinic anhydrous form). The data for these four solubility curves follow, the composition of the solution being given, as is customary, in weight per cent of Na_2SO_4 present, irrespective of the nature of the solid phase.

This system shows the phenomenon of suspended transformation to a marked extent, as indicated by the dotted lines in the diagram.

The solubility curve for the decahydrate BF has been carried some distance beyond the transition temperature of 32.4°, to the point F'. Here, as in all cases of solubility, the solubility of the metastable body is higher than that of the stable body, so that if a crystal of the anhydrous salt is put into the solution of the composition F', the solubility drops to F with a simultaneous drop of temperature, since the precipitation of the solid is an endothermic reaction. The solubility curve of the rhombic anhydrous salt, GF, has also been prolonged

a considerable distance into the metastable region, as shown by *FD*, and the ice curve *AB* has been extended to *C*. In this metastable region to the left of *BF* a second hydrate, of the formula $Na_2SO_4.7H_2O$, has been found, having a solubility curve *CE*; it is itself metastable and gives rise to a metastable eutectic with ice at − 3.55° (C.) and a metastable transition point to the decahydrate, *E*, at 24.2°. The data for this curve are given as the last part of Table XXV-A.

TABLE XXV-A

THE SYSTEM: SODIUM SULFATE-WATER

Solid Phase: Ice (*AB*) [1]		Solid Phase: $NaSO_4.10H_2O$ (*BF*) [2]		Solid Phase: Na_2SO_4 Rhombic (*FG*) [3]	
Temp.	Per Cent Na_2SO_4 in Solution	Temp.	Per Cent Na_2SO_4 in Solution	Temp.	Per Cent Na_2SO_4 in Solution
− 0.6°	1.96	0°	4.76	35°	33.4
− 1.2	3.85	10	8.3	50	31.8
		20	16.3	100	29.8
		30	29.0	190	30.4
		32.7	33.6	234	31.0

Solid Phase: Na_2SO_4 Monoclinic (*GH*) [3]		Solid Phase: $Na_2SO_4.7H_2O$ (*CE*) [2]	
Temp.	Per Cent Na_2SO_4 in Solution	Temp.	Per Cent Na_2SO_4 in Solution
250°	29.5	0°	16.3
279	25.3	5	19.4
319	17.2	10	23.1
		15	27.0
		20	30.6
		25	34.6

[1] de Coppet, *Ann. chim. phys.*, (4) **25**, 539 (1872); *Z. physik. Chem.*, **22**, 239 (1897).
[2] Seidell, Solubilities, N. Y., 1919, p. 667.
[3] Wuite, *loc. cit.*

The complete system, $Na_2SO_4 - H_2O$, shows the five quadruple points as invariant points *B*, *C*, *E*, *F* and *G*. *B* and *C* will be recognized at once or eutectics. *E*, *F* and *G* are transition points, of which we will discuss one (*F*) in some detail. The point *F* represents the stable transition point of the decahydrate to the rhombic anhydrous form, the phase reaction being the following: $Na_2SO_4.10H_2O \rightleftharpoons Na_2SO_4$ + solution. The change from left to right represents a partial fusion, since the solid hydrate changes to a solution plus a second solid; such a transition is sometimes called an *incongruent melting point*, to distinguish it from a true or congruent melting point, which will be discussed with our next type of system. While not a melting point in the exact sense, it is nevertheless a change of great practical usefulness, since it occurs at an invariant temperature and therefore gives a convenient means of obtaining a

definite and constant temperature. If a sample of the hydrate be subjected to the influence of a higher temperature, it will maintain this constant temperature F until the transformation is complete. Richards [1] has found the temperature to be 32.383°, as carried out in an open vessel; this is not exactly the quadruple point, which by definition must be under the natural vapor pressure of the system, and has been found to be 32.6°.[2] The transition points of this and other hydrates give us one of our most convenient methods of obtaining fixed points for the standardization of thermometers.[3] Such transition points are also of use in making constant-temperature baths for experimental work. Further, since the transition from anhydrous salt to hydrate is an exothermic change, such materials find use as thermophores or heat-producing mixtures for warming purposes; thus, a quantity of sodium acetate and water, if heated above its transition point and allowed to cool, forms a metastable saturated solution of the anhydrous salt and water, but, upon crystallization of the stable hydrate being started by agitation or other means, the temperature will rise to the transition temperature (58°) [4] of the compound $NaC_2H_3O_2.3H_2O$ and remain at that temperature until all the heat of transformation has been evolved.

We shall consider next the vapor-pressure relations of this system. In the first place, it should be stated that for a two-component system there can be no such thing as the vapor pressure of a single solid such as $Na_2SO_4.10H_2O$, for if we imagine a vessel containing only this solid and water vapor there are but two phases present, so that the system is bivariant and any vapor pressure may be maintained within certain limits. It is only when three phases are present that the system becomes univariant and has a definite vapor pressure for each temperature, and this vapor pressure will depend upon which choice of three phases is present. We must consider then the vapor pressures of all the various phase-complexes, and not the indefinite pressures of a single compound or solution. The three-phase univariant systems with the two components sodium sulfate and water (omitting the heptahydrate from consideration because of its metastability, and the monoclinic anhydrous form because of the high temperatures required) are the following, vapor phase being assumed present in each instance: $S_r - L - V$, $S_{10} - S_r - V$, and $S_{10} - L - V$. In Fig. 18 these three curves are shown schematically; the solution phase is in each case the saturated solution, since only when saturated can it remain in equilibrium with the solid phase. The continuous curve ACB is the curve for the pressure of the system consisting of rhombic anhydrous salt and saturated solution; it rises with temperature rise, and is here shown for temperatures both below and above its transition point C at 32.4°. Considering next the

[1] Richards, *Z. physik. Chem.*, **26**, 690 (1898); Richards and Wells, *ibid.*, **43**, 465 (1903); Dickinson and Mueller, *J. Am. Chem. Soc.*, **29**, 1381 (1907).

[2] Cohen, *Z. physik. Chem.*, **14**, 90 (1894).

[3] Richards, *loc. cit.;* Richards and Churchill, *ibid.*, **28**, 313 (1899); Richards and Wells, *loc. cit.;* Richards and Wrede, *ibid.*, **61**, 313 (1908); Richards and Fiske, *J. Am. Chem. Soc.*, **36**, 485 (1914).

[4] The transition point is very close to the metastable conjugate melting point; Green, *J. Phys. Chem.*, **12**, 655 (1908); Miller, *ibid.*, **12**, 649 (1908).

curve for the decahydrate and saturated solution, it must, at the lower temperatures where it is in stable equilibrium, have a higher vapor pressure than the first system, since the concentration of salt in its saturated solution is less than in the metastable solution; we must represent it therefore by a point D, above A. This curve also will rise with rising temperature and must pass through the point C, since at that temperature the same solution is saturated with respect to both solid phases; the two systems could not have different vapor pressures, otherwise, vapor would distill from one to the other, or, in other words, the two systems would not be in equilibrium. The curve DC therefore lies above AC throughout; and it should be pointed out that there is no inconsistency in the stable system having the higher vapor pressure, but that, for a two-component system where solutions are present, the higher vapor pressure for the stable system is a necessity. The third system, consisting of the two solid phases and vapor, has the lowest vapor pressure, which is represented by EC; it is a stable system below 32.4°, for certain ranges of composition as shown in the upper left-hand corner of Fig. 17. This curve also must pass through the quadruple point C, since at that temperature the two solids are not only in equilibrium with each other but are also in equilibrium with solution, and hence must show the same vapor pressure as systems including the solution. The complete diagram shows one three-phase system stable above 32.4° and two systems stable below; above that temperature there is therefore only one stable equilibrium vapor pressure possible for three phases, while below it there may be either of two. Which of these two will prevail at a given temperature is solely a question of the total quantities present in the system. Let us suppose that, in a desiccator at room temperature, is put a large quantity of anhydrous Na_2SO_4 as a drying agent and above it a dish containing a small amount of saturated solution including crystals of $Na_2SO_4.10H_2O$; in that case the total composition will be represented by the point x in Fig. 17. The vapor pressure of the system $S_{10} + L$ (DC in Fig. 18) is higher than that of $S_{10} + S_r$ (EC in Fig. 18); vapor at the higher pressure will therefore hydrate the anhydrous desiccating agent, forming the system of lower vapor pressure, and the solution will evaporate completely, leaving pure $Na_2SO_4.10H_2O$ on the dish under a pressure on the line EC (Fig. 18). Such a system can be used to obtain a hydrate of definite composition for analytical purposes.[1] If, on the other hand, the amount of anhydrous Na_2SO_4 taken were small, so that the total composition is that of y in Fig. 17, it would be completely hydrated before the solution is evaporated, and the higher vapor pressure represented by DC (Fig. 18) would prevail.

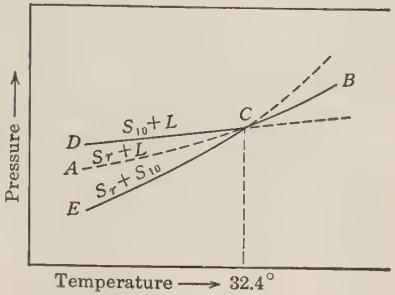


FIG. 18. *p.-t.* Diagram for the System, Sodium Sulfate-Water (Schematic)

[1] Hill and Smith, *J. Am. Chem. Soc.*, **44**, 546 (1922).

IIb. Compounds as Solid Phases, with Congruent Melting Point: In a large number of systems in which additive compounds exist, it is found that these compounds not only possess a transition point such as has been described above, but also possess the property of melting sharply and distinctly into a liquid of the same composition as the solid. Such bodies are said to possess a *congruent melting point*, and possess a solubility curve quite different from those previously discussed. Phenol and aniline fall into this class, and will serve as our example. In this system three different solid phases appear, namely, aniline, phenol, and a compound of the formula $C_6H_5NH_2 . C_6H_5OH$. These give rise to three solubility curves which are represented in Fig. 19 by the three curves *de*, *ab*, and *bcd*; the data follow from which the curves are drawn.

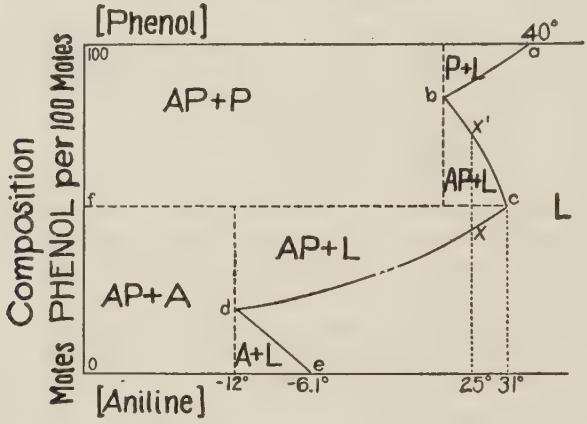


FIG. 19. The System, Phenol-Aniline (Schematic)

The composition of the solutions is given in molar percentages, which is always the most logical method of representing composition and is here of especial convenience where the composition of compounds is to be deduced. The point *d* in Fig. 19 is a eutectic, from which originates the solubility curve for the compound, *dc*; the solubility increases with temperature up to 31° and a composition of 50 per cent molar of aniline and of phenol, that is, a 1 : 1 molar ratio. This is, from the diagram, the point of maximum temperature at which the compound can exist in equilibrium with solution; the solution, it will be seen, has here the same composition as the solid. This point, invariant in that there are present three phases and that the restriction is imposed that solution and solid shall have the same composition, is the congruent melting point: it is also spoken of as a *dystectic*, in contradistinction to a eutectic, it being the highest melting point and the eutectic the lowest. From *c* the curve is retrograde to the point *b*, which is a second eutectic with compound and phenol as the two solid phases.

TABLE XXVI

THE SYSTEM: ANILINE-PHENOL[1]

Aniline in Solution in Moles per 100 Moles

Solid Phase: Aniline (*de*)		Solid Phase: Compound (*bcd*)		Solid Phase: Phenol (*ab*)	
Temp.	Composition	Temp.	Composition	Temp.	Composition
− 6.1°	100 *c*	(− 12°)	( ) *d*	(15°)	( ) *b*
− 7.1	98.5	− 5.2	89.2	18.5	20.4
− 8.1	96.9	+ 5.7	83.7	25.3	15.4
− 9.5	94.8	22	70.1	29.5	11.6
− 11.4	92.4	27.5	60.9	32	9.8
− (12)	( ) *d*	29.5	55.5	35	6.5
		(31)	(50.0) *c*	37.3	4.0
		29.9	45.2	(40)	0.0 *a*
		27.7	37.3		
		24.9	33.3		
		18	25.4		
		16.2	23.4		
		(15)	( ) *b*		

[1] Schreinemakers, *Z. physik. Chem.*, **29**, 581 (1899).

A curve of this character, showing a maximum temperature and a retrograde direction upon one branch, is considered proof of both the occurrence and the composition of a compound;[2] the composition is read directly from the ordinate (here 1 : 1 of phenol and aniline) and is therefore known without the necessity for the isolation and analysis of the solid. In many cases the separation of a solid for analysis is difficult or impossible; in such cases the phase-rule evidence is invaluable. Our knowledge of compound formation in alloys, for example, is very largely based upon evidence of this type.

It will be at once observed that, at certain temperatures, such as 25° in the above case, there are two solutions, x and x' respectively, which can be in equilibrium with the same solid phase (here the compound, abbreviated as AP) at the same temperature. This paradox finds a simple explanation if we look upon our diagram as showing two systems and divided along the line fc; considering now the upper half, it shows the two-component system, phenol-compound, with a perfectly regular pair of freezing-point curves such as were given earlier in Fig. 14. The choice of these two components is entirely permissible, since the composition of all the phases may be expressed in terms of the two; and the freezing-point curve of the compound (cb) shows the usual depression of freezing point with addition of the second component, phenol. In like fashion the lower half of Fig. 19 represents the system aniline-compound, and the freezing point of the compound is lowered by the addition of aniline. Returning to the complete figure, the freezing point of the com-

[2] An exception to this reasoning is the occurrence of a maximum freezing point of a *solid solution*, which will be discussed later.

pound is lowered by either aniline or phenol, as it would be with any component, whether or not that component could enter into its own composition. Any system showing congruent melting points may be resolved, for purposes of interpretation, into a number of two-component systems along the lines of the composition of the congruently melting compounds.

In the study of systems composed of a salt and water, many examples of hydrates are found which melt congruently and have diagrams built upon the type of Fig. 19. Thus, to mention a few, the hydrate $Na_2S_2O_7.5H_2O$ melts congruently at 56°, and $NaC_2H_3O_2.3H_2O$ at 58°; calcium chloride forms the hydrates $CaCl_2.6H_2O$, $CaCl_2.4H_2O$ (alpha form), $CaCl_2.4H_2O$ (beta form), $CaCl_2.2H_2O$ and $CaCl_2.H_2O$, of which only the hexahydrate [1] melts congruently. The system ferric chloride-water [2] is perhaps the most striking instance of multiple congruent melting points. There are four stable hydrates, $Fe_2Cl_6.12H_2O$,[3] $Fe_2Cl_6.7H_2O$, $Fe_2Cl_6.5H_2O$ and $Fe_2Cl_6.4H_2O$, all possessing congruent melting points. The detailed solubility data will be omitted, but the temperatures and compositions at the six eutectics and the four congruent melting points are given below. Fig. 20 represents the system graphically.

TABLE XXVII

THE SYSTEM: FERRIC CHLORIDE-WATER

Point (Fig. 20)		Temperature	Solid Phases	Moles Fe_2Cl_6 per 100 Moles H_2O
M.P.	*A*	0°	Ice	0
Eutectic	*B*	− 55	Ice : $Fe_2Cl_6.12H_2O$	2.75
Dystectic	*C*	+ 37	$Fe_2Cl_6.12H_2O$	8.33 (=1: 12)
Eutectic	*D*	27.4	$Fe_2Cl_6.12H_2O$: $Fe_2Cl_6.7H_2O$	12.15
Dystectic	*E*	32.5	$Fe_2Cl_6.7H_2O$	14.29 (=1: 7)
Eutectic	*F*	30	$Fe_2Cl_6.7H_2O$: $Fe_2Cl_6.5H_2O$	15.12
Dystectic	*G*	56	$Fe_2Cl_6.5H_2O$	20.00 (=1: 5)
Eutectic	*H*	55	$Fe_2Cl_6.5H_2O$: $Fe_2Cl_6.4H_2O$	20.32
Dystectic	*J*	73.5	$Fe_2Cl_6.4H_2O$	25.00 (=1: 4)
Eutectic	*K*	66	$FeCl_6.4H_2O$: Fe_2Cl_6	29.2
Eutectic	*M* (metastable)	15	$FeCl_6.12H_2O$: $Fe_2Cl_6.5H_2O$	

In systems like the above, in which only one of the components is appreciably volatile (here the water), very interesting phase changes occur upon isothermal evaporation. Let us assume that an unsaturated solution of ferric chloride and water be maintained at a constant temperature of 31°; the point is represented by x in Fig. 21. If it be allowed to evaporate at this temperature, all changes that occur will be represented by the intersection of the isotherm at 31° with the various solubility curves. As water evaporates, the solution becomes more concentrated, until at the composition 1 it begins to precipitate $Fe_2Cl_6.12H_2O$. The composition of the solution, which is now saturated, of course remains constant until it has completely evaporated, leaving only solid behind; meantime, the total composition

[1] Roozeboom, *Z. physik. Chem.*, **4**, 31 (1889).

[2] Roozeboom, *ibid.*, **10**, 477 (1892).

[3] The double formula Fe_2Cl_6 is used in order to avoid fractional coefficients for the water.

has risen to the point 2, which is the composition of the hydrate. As water now leaves the hydrate by evaporation, solution of the composition 3 begins to appear, increasing in amount until the whole mass has liquefied and has the composition of the point 3; that is, by removal of water isothermally, the solution x has first changed completely to solid and then changed completely to liquid. Following the isotherm upward, at the points 4, 5 and 6 the process

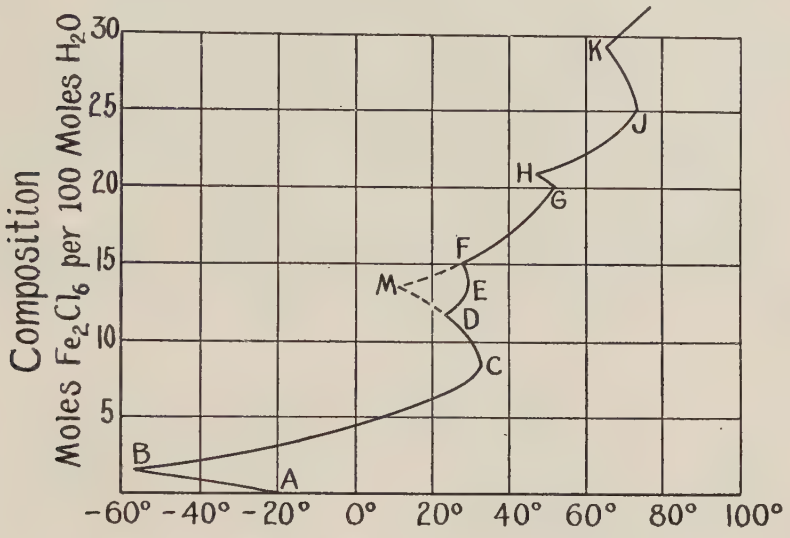


FIG. 20. The System, Ferric Chloride-Water (Schematic)

is again repeated in detail, and at 7 there is a third solidification which is not again followed by liquefaction. These remarkable changes, which find simple representation in a phase-rule diagram, would be quite inexplicable in the absence of the phase rule.

General Considerations Relative to Types Ia, Ib, IIa and IIb: Solubility curves such as those of type IIb, in which congruent melting points occur, have been shown to be of great value in determining the existence and composition of compounds. Such curves, for example, will determine beyond dispute in the case of optical isomers whether the inactive form is a racemic mixture or a racemic compound; in the first instance the freezing-point curves, or solubility diagram, will show a single eutectic only (as in Fig. 14), while in the latter case there will be two eutectics and a congruent melting point (as in Fig. 19). In this latter case the diagram will show perfect symmetry; inasmuch as optical antipodes show similar physical properties, the two melting points of the pure components will be the same, the slope of the two solubility

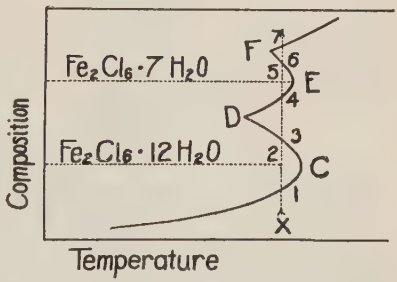


FIG. 21. Isothermal Evaporation in the System, Ferric Chloride-Water

curves will be the same, and, as a result, the two eutectics will have the same temperature; and the composition ratio at one of them will be simply the inverse of that at the other. The congruent melting point may be either higher or lower than the melting point of the pure components.

It will be apparent that systems may show the types of curves indicated for more than one type; thus calcium chloride and water show points of incongruent transition as well as congruent melting points, and the formation of two liquid phases is by no means restricted to systems showing only a single eutectic, like succinic nitrile and water (Fig. 16), but occurs as well where there are transition points and congruent melting points. However, any two-component system (excepting those in which solid solution occurs, which still remain to be discussed) can be treated as a combination of these four types; in short, solubility curves, transition points, eutectics, congruent melting points and melting points of components include all the phase relations affecting the solid-liquid equilibrium.

Eutectics for the system composed of salt and water have proven so useful for experimental work that an abbreviated list is given in Table XXVIII. Herewith are included, also, those for a few acids with water, and bases with water.

TABLE XXVIII

TWO-COMPONENT EUTECTICS

Component	Solid Phase, with Ice	Eutectic Temperature	Wt. Per Cent Component
Na_2SO_4	$Na_2SO_4.10H_2O$	− 1.2°	3.85
$MgSO_4$	$MgSO_4.7H_2O$	− 3.9	19
KBr	KBr	− 13	32.15
NH_4NO_3	NH_4NO_3	− 17.35	41.2
NaCl	NaCl (meta-stable)	− 22.4	23
NaCl	$NaCl.2H_2O$	− 21.2	22.4
$C_2H_4O_2$	$C_2H_4O_2$	− 26.75	58.9
$CaCl_2$	$CaCl_2.6H_2O$	− 55	29.9
$FeCl_3$	$FeCl_3.6H_2O$	− 55	33.1
$AgClO_4$	$AgClO_4.H_2O$	− 58	73
KOH	$KOH.4H_2O$	(− 70)	(32)
H_2SO_4	$H_2SO_4.4H_2O$	− 75	38
HCl	$HCl.3H_2O$	− 86	24.8

IIIa. Solid Solutions as Solid Phases; A Single Solid Solution Present: Abnormalities in the freezing-point curves of certain systems led van't Hoff [1] to the view that the solid being precipitated was not a pure component, but a solid phase of variable composition to which he gave the name *solid solution.* Brief reference to solid solution has been made in the section on the Distribution Law. A definition of such a substance is simple; it is to be viewed as a phase and therefore homogeneous, and of variable composition and therefore a solution, existing in the solid state. The concept of a solid solution occasionally gives difficulty, but if approached *de novo* it is no more difficult (and also no less difficult) than the concept of a liquid solution. It is the idea of homo-

[1] *Z. physik. Chem.*, 5, 322 (1890).

geneity in a body in which we know that there is more than one substance present that gives the difficulty; and it is true that to admit salt water as homogeneous is perhaps impossible philosophically and no less so if one prefers to think in terms of the molecular hypothesis. But salt water is homogeneous if defined empirically; that is, heterogeneity has not been demonstrated experimentally, and the treatment of it as homogeneous under the phase rule brings about no contradictions. In exactly the same manner, a solid solution is regarded as homogeneous for the same empirical reasons. The difficulty to the student has not been lessened by calling these solid solutions by the contradictory name of "mixed crystals," when the essential fact is that a solid solution is *not* a mixture of crystals, but a uniform, homogeneous phase.

In solid solution the condition is independent of the state of the pure components under the same temperature and pressure, just as for liquid solutions; that is, the phase is equally a solid and equally homogeneous whether it be made from a solid and a gas, a solid and a liquid, or from two solids. The property of solubility in the solid state is however much less common than in the liquid state, as has been previously pointed out, and of course less common than in the gaseous state, where all components are soluble.

In dealing with liquid solutions, we have learned that, in some two-component systems, the liquids show complete mutual solubility, giving rise to but a single liquid phase, while other systems, in which there is limited solubility, form two liquid phases bearing conjugate relation to each other. The same conditions prevail for solids; the two components may dissolve mutually in all proportions, forming only a single solid solution, or may possess limited solubility and form two solid solutions which are conjugate. Extending our use of the term conjugate beyond its application to two liquid solutions, it will be seen that we may have the conjugate relation between a liquid and a solid solution and also between two solid solutions. We shall give our attention first to cases where the conjugate phases are a liquid solution and a solid solution.

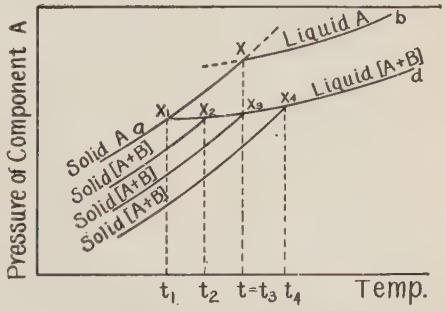


FIG. 22. Vapor Pressure of Component *A* in Solid and Liquid Phases

Our problem being to trace the course of the equilibrium between a solid (albeit a solid solution) and a liquid phase, it is obvious that, to show the changes of concentration with the temperature, a freezing-point curve can be constructed. In our previous attention to freezing-point curves we have assumed, in accordance with the laws of dilute solution, that the freezing point of a solid is always lowered by the presence of a second component in the liquid phase. This assumption is justified, by the laws of thermodynamics, as long as the solid phase is a pure component; but there is

no foundation for any such generalization when the solid phase is a solid solution. In this case, the freezing point of the solid solution may be either lower than that of the pure component, equal to it or higher, and all three possibilities are known. Fig. 22 is designed to demonstrate qualitatively these three conditions.

Let us consider the vapor pressure of the component A alone (i.e., its so-called partial pressure) in a system composed of A and B. The curve ax is the vapor-pressure curve of the pure solid and bx that of the pure liquid phase, the two intersecting at x; this relationship for a single component has previously been shown in Fig. 4. Let us now consider that the liquid phase has an amount of B added to it; the curve representing the vapor pressure of A in this solution must fall below the curve for pure liquid A, since the vapor pressure of A is always lowered by a second component. The curve for this solution, dx_1, intersects ax at the point x_1, and the point of intersection is the freezing point, at which the vapor pressure of A in the two phases is the same, that being a necessary condition for equilibrium. The point x_1 is, by the diagram, necessarily at a temperature t_1 lower than t, which accords with the rule that where the solid phase is the pure component its freezing point is always lowered by a second component in the solution. Let us now consider however that the solid phase which forms is a solid solution containing varying quantities of B; the curves representing the pressure of A in these solid solutions fall below ax a distance dependent on the amount of B present in the solid phase. The intersections of these curves for the solid phase with that for the liquid phase (dx_1) are the freezing points, where the pressure of A in both phases is the same; and it will be seen that, according as the solid phase contains little or much B, the freezing point is below $t(t_2)$, equal to it (t_3) or above it (t_4). As to the concentrations in the phases at these various points, it can be shown thermodynamically, as it has been shown experimentally, that the following rule holds; if the concentration of the second component is greater in the liquid phase than in the solid phase, the freezing point is lowered (x_1 and x_2), and if it is greater in the solid phase, the freezing point is raised (x_4).

What has been shown for solid solutions in which A is the predominating component may also be shown where B predominates; it follows then that in a general system $A - B$ where solid solution occurs, the freezing point of each solid phase may be lowered, the freezing points of each may be raised, or one may have its freezing point raised and the other have it lowered.[1] There will therefore be three types of curves necessary to express these three cases.

Let us now recapitulate what has been learned about systems consisting of a liquid phase and single solid solution, so that we may be in position to interpret complete diagrams: (1) there will be a liquid solution and solid solution bearing a conjugate relation to each other, and of course two separate curves will be necessary to show the composition of these two phases; (2) since only one solid phase and one liquid phase have been postulated, and only one vapor phase is possible, there can not be more than three phases present, and no invariant points, which require four phases (eutectics, transition points, etc.), can appear; (3) the freezing points of a pure component may be either raised or lowered by the second component, giving rise to three types of curves.

In Fig. 23 have been drawn schematic representations of complete systems

[1] The special case in which freezing points are neither raised nor lowered will not be discussed in detail; the two optically active oximes of camphor offer an example of this case.

fulfilling these requirements. Curve I illustrates the case where each component has its melting point lowered by the second. The curve *agcfe* represents the composition of the liquid phase, and is called the *liquidus curve;* the dotted line *abcde* is the curve for the solid phase, called the *solidus curve*, and the tie-lines show the conjugate relation. The position of these two curves with reference to each other fulfills the rule developed above; at a given temperature t the liquid phase f contains more of A than does the solid phase d which therefore has a lower melting point than that of pure $B(e)$, and likewise the

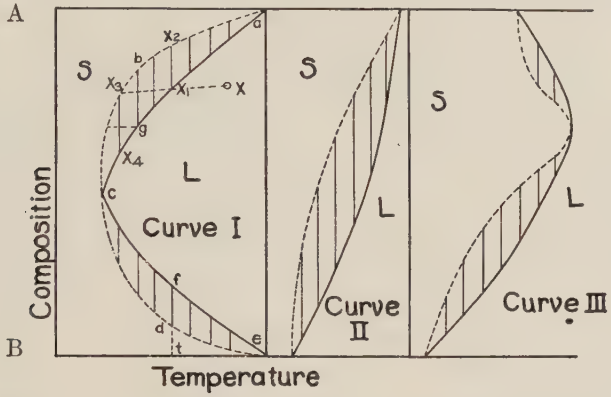


FIG. 23. The System A-B; Solid Phase, a Single Solid Solution

liquid g contains more of B than does the solid phase b, in accordance with which its melting point is lower than that of pure $A(a)$. The point c bears a superficial resemblance to a eutectic, but is in no sense to be regarded as such, since it is not a four-phase point; it is correctly described as a minimum melting point, which is a characteristic point in systems of the type in which each component has its melting point lowered by the other. It should be noted that the three types of curves shown in Fig. 23 are similar to the boiling-point curves shown in Figures 10*a*, 10*b* and 10*c*, for systems consisting of gaseous and liquid solutions in equilibrium.

Information as to the melting and freezing points in such a system can be gained by following an isopleth from the point x toward lower temperatures. Starting with this composition and temperature, the mass is liquid until the temperature of x_1 is reached; here solid appears, but of the composition x_2, as indicated on the tie-line $x_1 - x_2$, and it is apparent that the solid will be relatively rich in A and the liquid rich in B. If now the temperature be allowed to fall, the isopleth crosses tie-lines joining all compositions of solid from x_2 to x_3, and all compositions of liquid from x_1 to x_4; the solid will therefore be increasing in amount and in concentration of B along the line $x_2 - x_3$ and the liquid decreasing in amount and also increasing in concentration of B along $x_1 - x_4$, so that the last drop of liquid has the composition x_4 and the total solid the composition x_3. If the temperature be halted between x_1 and x_3, fractional crystallization can be effected; this will be discussed later. The temperature x_1 is the temperature at which, for this composition, solid first appears, and is spoken of as the freezing point of that complex; by extension, the whole liquidus curve is regarded

as a freezing-point curve. On the other hand, the point x_3 is the point at which liquid first appears on rising temperature, and is called the melting point, so that the solidus curve is a melting-point curve. For such a system it is clear that the terms melting point and freezing point represent entirely different temperatures; it is only where a solid liquefies to form a liquid phase of the same composition as itself that the term melting point and freezing point are interchangeable, as in the case of a one-component body or a compound melting congruently.

Mercuric bromide and iodide give curves represented by Curve I, Fig. 23, with a minimum point at 59 per cent $HgBr_2$ (molar) and 216.1°. The small inconsistencies at 100 per cent $HgBr_2$ and 0 per cent $HgBr_2$, as well as at the minimum point, represent experimental error.

TABLE XXIX

THE SYSTEM: MERCURIC BROMIDE-MERCURIC IODIDE [1]

Molar Per Cent $HgBr_2$	Freezing Point (Liquidus Curve)	Melting Point (Solidus Curve)
100	236.5°	236°
90	228.8	226
80	222.2	219
70	217.8	217
60	216.1	215.5
50	217.3	216
40	221.1	218
30	227.8	223
20	236.2	231
10	245.5	242
0	255.4	254

[1] Reinders, *Z. physik. Chem.*, **32**, 494 (1900).

The other two types of curves obtained are shown in Fig. 23 as Curves II and III. Curve II represents the case where the melting point of A is depressed by B, but that of B raised by A; hence the liquid phase at all temperatures is richer in B than is the solid phase, to account for melting points lower than that of A, or to state the same condition differently, the solid phase is richer in A than is the liquid phase, to account for melting points higher than B. Curve III represents the elevation of the melting points of both components, leading to a maximum melting point; the position of the liquidus and solidus curves will be found to accord with the rule relating to concentrations in the two phases with the rise in freezing point. Instances illustrating Curves II and III are known. In general, complete mutual solubility of the solids leading to systems represented by these three curves are not very common, and naturally enough occur most frequently where the two components are closely related, as benzene and thiophene (Table IX), mercuric iodide and bromide (Table XXIX), metals of like character or optical isomers.

IIIb. Solid Solutions as Solid Phases; Two Solid Solutions Present: When the two components show a limited solubility in the solid phase, a number of new relations appear. In the first place, these two solid solutions will bear a conjugate relation to each other. Secondly, if the temperature limits of this conjugate curve extend up to the temperatures where liquids exist, there will

be two solids and a liquid coexisting which, with the vapor phase, make four phases and give rise to an invariant point which meets the definition of a eutectic or transition point. Further, either of these solid solutions alone may be in conjugate relation to the liquid phase giving rise to conjugate solidus-liquidus curves such as have been shown in Fig. 23. The conjugate relationship of the two solid phases will be discussed under a later heading, the relationships with the liquid phase being our present topic.

When the solidus-liquidus curves show a minimum melting point, like that of Fig. 23, Curve I, the existence of two solid solutions produces a eutectic at this point; the condition is shown in Fig. 24. Here the liquid of minimum freezing point, *b*, is in equilibrium with the two solid solutions of composition *d* and *e*, as shown by the tie-line *dbe*. This corresponds to a eutectic. Indeed, the system may be compared with the simplest melting-point diagram, that of Fig. 14, and the single distinction is that the liquid phase in Fig. 24 is conjugate with solid solutions, represented by *aef* and *cdg*, whereas in Fig. 14 it is conjugate with the pure components. Potassium nitrate and thallium nitrate [1] are an example of this class.

When the solidus-liquidus curves rise from the melting point of one component to that of the second, the system may be represented by Fig. 25. Here

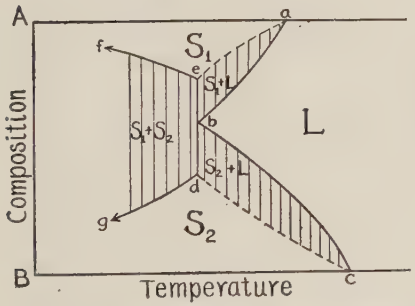


Fig. 24. The System A-B; Solid Phases, Two Solid Solutions with Eutectic

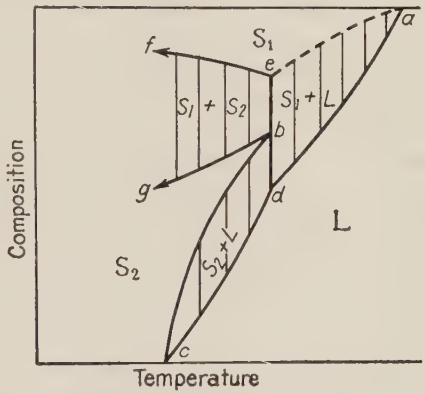


Fig. 25. The System A-B; Solid Phases, Two Solid Solutions with Transition Point

the juncture of the conjugate curve for the solid solutions (*fe* − *gb*) with the conjugate solid-liquid curves (*ad* − *ae*) produces an invariant condition where the phases are the two solid solutions *e* and *b*, the liquid solution *d* and vapor. This corresponds to a transition point, as shown earlier in Fig. 17; it is marked by the appearance of a new solid phase, whether one cools the system $S_1 + L$ or warms the system $S_2 + L_1$, and by a discontinuity of the solubility curve at *d*. Silver nitrate and sodium nitrate [2] offer an illustration of this type of

[1] Van Eyk, *Z. physik. Chem.*, **30**, 430 (1899).
[2] Hissink, *Z. physik. Chem.*, **32**, 542 (1900).

curve; the transition temperature t is 217.5°, at which temperature the liquid d contains 19.5 per cent molar of sodium nitrate, and the solid solutions b and e 26 per cent and 38 per cent respectively.

General Consideration of the Solid-Liquid Equilibrium: The various systems that have been illustrated in the study of solid-liquid equilibrium require as experimental data a solubility curve in every case; that is, knowledge of the composition of the liquid phase at each temperature and likewise knowledge of the composition of the solid phase in equilibrium with it. The experimental methods for determining the composition of the liquid may again be classed as plethostatic and thermostatic. Among plethostatic methods the most commonly used is the so-called freezing-point method of Beckmann, which needs no description here; by it the temperature is determined at which solid phase begins to appear from a liquid complex of known composition. Similar in principle but less delicate in execution is the method of sealing the known complex in a closed tube, lowering and raising the temperature of a surrounding bath and observing the temperature at which the solid phase appears and disappears; the method can be used at high temperatures at which the materials would disappear by boiling if in open vessels. Thermostatic methods are conducted by stirring or otherwise agitating materials at a fixed temperature until equilibrium has been obtained and then withdrawing a sample of the solution for analysis.

These reliable and well-known methods give data as to the composition of the liquid phase, but give no information at all as to the saturating solid phase. In some instances the solid phase can be removed by filtration and prepared for analysis; but it should be remarked that this procedure requires careful control and, in general, some considerable previous knowledge of the system if error is to be avoided. Such a solid phase is of course always wet with liquid, the complete removal of which is necessary before analysis. The process of removal, and the temperature control of the work must be such that no change in the solid phase occurs; and where the solid is, for example, a hydrate or other compound containing a volatile component, changes in composition are not always easy to avoid. For that reason certain indirect methods of determining the composition of the solid are often more reliable. One such indirect method has already been indicated; where the solid phase is a compound with a congruent melting point, its composition may be taken from the diagram (see Fig. 19) and is the same as that of the coexisting liquid phase.

A second method proposed by Bancroft[1] consists in adding to the system of the two components A and B a small known amount of a third component C which does not enter the solid phase; the ratio of A to C in this complex is written x_1 and that of B to C as y_1. Upon cooling to the temperature at which a solid phase has appeared, the liquid is again analyzed and the ratio of A to C recorded as x_2 and that of B to C as y_2. The change in the ratio of A to C represents the amount of A that has gone into the solid and is therefore $x_1 - x_2$, while $y_1 - y_2$ represents the amount of B which has entered the solid phase; the formula, if it be a compound, is accordingly $(x - x_2)A.(y_1 - y_2)B$. If the solid is a solid solution instead of a compound, its composition is also correctly given, but a second experiment

[1] Bancroft, *J. Phys. Chem.*, 6, 178 (1902).

with altered concentrations of A and B taken must of course give an altered composition of the solid solution.

By all means the commonest method however of determining the nature of the solid is by a study of the cooling curve for the system, a method proposed by Tammann [1] and almost universally used in the study of alloys, where the mechanical isolation of a solid phase is out of the question. It is clear that if a heated system is allowed to cool with a constant outside temperature environment, the loss of heat will depend upon the heat radiation of the system as a whole, including the container, and the heat changes occurring within the system as a result of alteration in the chemical equilibrium with the temperature. Keeping these two factors in mind, let us plot schematically a cooling curve for a system like that of Fig. 14, starting with a complex x; in Fig. 26 we will plot the results, using time and temperature as coördinates. The system is composed of liquid and vapor and is therefore bivariant, so that its temperature may fall without producing any phase reaction; the cooling curve therefore beginning at a will be a smooth curve. At the temperature at which the solution reaches saturation however, solid phase appears and heat is produced by that phase reaction so that the direction of the cooling curve is altered and the rate of cooling lessened; b, the point of discontinuity, is the saturation temperature. The system now consists of three phases and is univariant, permitting the fall of temperature to continue until the eutectic temperature is reached; here occurs, at c, a second discontinuity in direction, and what is most important, the temperature will remain constant (the system being now of four phases and invariant) until the liquid has entirely disappeared, the positive heat of formation of the eutectic solids compensating for the loss of heat by radiation. When the liquid has finally disappeared, the system becomes univariant and a cooling curve de for the solids follows.

The cooling curve has revealed certain " arrests," b and c, indicating temperatures pertinent to the study of the system; by repetition under altered circumstances it may also be

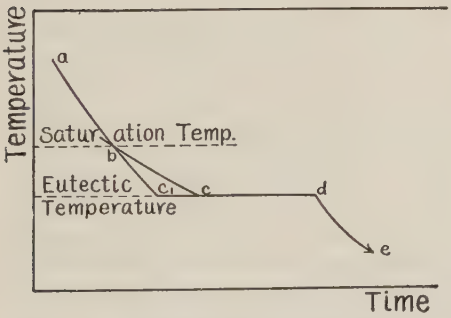


Fig. 26. Cooling Curve for a Two Component System

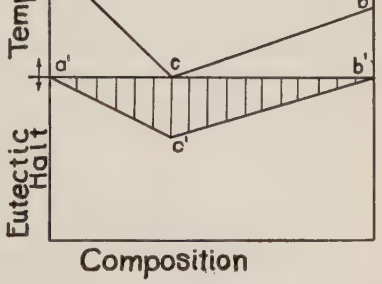


Fig. 27. Eutectic Halt, Showing Composition of Eutectic Solids

[1] *Z. anorg. Chem.*, **37**, 303 (1903); **45**, 24 (1905).

made to reveal the desired composition of the solid phase. It is the time of the eutectic halt (i.e., the time interval $c - d$) which may be made to give this information. It is obvious that the duration of the eutectic halt depends upon the quantity of liquid components which change to solid and thus produce the heat which halts the cooling. If amounts of A and B of the same total weight as in the first experiment be taken, but now of the eutectic composition as y in Fig. 14, there will be no "arrest" at any point until the eutectic temperature is reached and the halt will be extended to its maximum, namely, cd, Fig. 26. That composition therefore which gives the maximum eutectic halt establishes the composition of the solid phases at the eutectic. In like manner, a halt will occur at other invariant points, such as a transition point; but if a composition of a compound having a congruent melting point is taken, there will be no eutectic halt, since, as previously pointed out, such a compound acts like an independent component and can therefore have no eutectic. The relationship of the eutectic halt to the composition of these solid phases is rendered clearer by Figs. 27 and 28, in which the duration of the eutectic halt with the composition is plotted directly below the temperature-composition plot; it will be seen that the maximum eutectic halt shows the eutectic composition, and zero eutectic halt shows the composition of pure components and congruently melting compounds. By more extended thermal methods it becomes possible to determine the composition of compounds which do not melt congruently and of solid solutions as well; such methods have been invaluable in the study of metallography.[1]

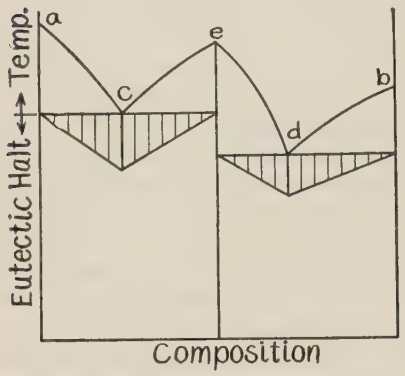


FIG. 28. Eutectic Halt, Showing Composition of Compound and of Eutectic Solids

Another general consideration of interest is the purification of solids by crystallization. Recrystallization of salts from water or of organic compounds from proper solvents is of course a common procedure; it should be noted however that in each of these operations the purpose is to purify from some relatively small quantity of a third component. The separation of a pure substance from a two-component complex is by no means so commonly practiced, nor perhaps so well understood; indeed the separation of two substances by distillation rather than crystallization is employed, not infrequently to the disregard of this simpler method. For purposes of comparison, it may be stated that most substances are volatile, and that therefore a distillation will in the majority of cases yield a vapor consisting of both components, so that tedious fractional distillation is necessary in order to obtain either component reasonably pure; on the other hand, since most substances are mutually insoluble in the solid state, in the majority of instances a pure component can be separated from a two-component solution by the simple process of cooling, and only occasionally is fractional crystallization necessary. With compressed carbon dioxide generally available, temperatures as low as [2] $-78°$ (its sublimation pressure under one atmosphere pressure) are conveniently obtained, and, in many localities, liquid air is available for production of temperatures down

[1] See Kremann, Die Anwendung der Thermsichen Analyse, Stuttgart, 1909.

[2] Thiel and Caspar, *Z. physik. Chem.*, **86**, 257 (1914).

to − 180°, so that the conditions for the separation of many substances by crystallization are not difficult to secure. If the substances used solidify as pure components or compounds, as in the systems illustrated by Figs. 14 to 20, it is necessary only to bring the total composition to a point on the desired side of the eutectic composition, and then to cool the system, stopping however above the eutectic temperature so as not to precipitate the second solid phase. The impurity (i.e., the second phase) is now on, but not in, the second phase; the solid retains the solution possibly by occlusion between crystals, or adsorption upon the surface. Good mechanical separation (the centrifugal machine is invaluable for this purpose) will leave traces only of solution present and a second crystallization of a sample so nearly pure will frequently give material of the highest purity. The usefulness of this method of separating organic compounds, such as various isomers, has not yet been sufficiently realized.

When, however, the solid phase which forms is a solid solution, it is necessary to resort to a fractional crystallization, just as it is usually necessary to resort to fractional distillation to separate by means of the vapor phase. The nature of the work of a fractional crystallization will be briefly explained.

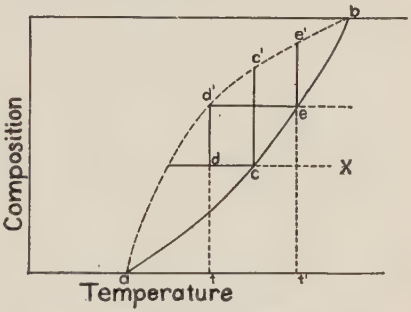


FIG. 29. Fractional Crystallisation

In Fig. 29 is shown a section of a diagram for a system having solid solutions; it is entirely immaterial what section of a complete diagram it be taken to represent, except in so far as a represents a point of lower temperature, such as the minimum melting point of Curve I, Fig. 23, or the melting point of the pure component in Curve II or III, while b represents a point of higher temperature such as the maximum melting point of Curve III or a melting point of a component. Let a complex x (Fig. 29) be cooled; at c, the freezing point on the liquidus curve, solid begins to appear. Let the complex now be cooled only to the point d, corresponding to the temperature t, at which the system will be only partly solid; the solid phase will now have the composition d'. If these crystals be filtered off, melted and cooled, crystallization begins at the higher temperature t', and the second crop of crystals will have a composition c' between d' and e', depending on the point at which crystallization is arbitrarily stopped. The crystals obtained are therefore approximating the composition b with repeated fractionation, and the liquid is therefore approximating a; how easily or how completely they may be brought to these compositions depends of course on the relative positions of the liquidus and solidus curves for the system, just as a fractional distillation depends on the partial pressures of the components and the positions of the boiling-point and condensation curves.

If now we compare the section used in Fig. 29 with the complete curves of Fig. 23, the following generalization may be made: by a fractional crystallization where solid solution occurs, the solid phase may be brought to the composition of the maximum freezing point, if such exists, or to that of a pure component, while the liquid phase may be brought to the composition of the minimum freezing point, if such exists, or to that of a pure component.

D. The Equilibrium Gas-Solid

Of the three possible diagrams to represent the equilibria between gaseous and solid phases, namely, the pressure-composition (*p-c*), pressure-temperature (*p-t*) and temperature-composition (*t-c*) diagram, we shall select the first two as most instructive, and as an example will choose a system consisting of a salt and water, where hydrate formation occurs. If we keep the water small enough in amount so that no liquid phase occurs, the possible phases consist of water vapor, anhydrous salt, and as many hydrates as occur. Copper sulphate forms a number of hydrates, namely, $CuSO_4.H_2O$, $CuSO_4.3H_2O$ and $CuSO_4.5H_2O$. Let us examine first the pressure-temperature relations, and insert them in Fig. 30. It must be stated that anhydrous $CuSO_4$ may be kept in contact with water vapor of certain pressures and temperatures without the slightest formation of a hydrate—a fact of primary importance in freeing our minds from the erroneous impression that this compound (or any substance) is a perfect dehydrating agent. The diagram therefore shows an area for the bivariant equilibrium $CuSO_4 + H_2O$, within which both pressure and temperature may be altered simultaneously without altering the number of phases; the formulæ $CuSO_4$ + vapor are printed in this area. If, however, the pressure of water vapor is increased, there comes, for each temperature, a point at which the hydrate $CuSO_4.H_2O$ forms; since three phases are now present, the system is now univariant, and the curve *OC* represents the pressures and temperatures for that equilibrium. The curve is commonly spoken of as the dissociation curve for the monohydrate, since it represents the dissociation pressure of the reaction $CuSO_4.H_2O \rightarrow CuSO_4 + H_2O$ (vapor). If we desire to speak of it as a vapor-pressure curve, it is the vapor-pressure curve for the system $CuSO_4.H_2O - CuSO_4 -$ vapor, and not, correctly speaking, for the hydrate alone; for this hydrate has no vapor-pressure curve, but, on the contrary, a vapor-pressure area above the curve. In this area, again, the two-phase system is bivariant, and is bounded above by the vapor-pressure curve for the system $CuSO_4.H_2O - CuSO_4.3H_2O -$ vapor. The other areas and vapor-pressure curves may be read from the figure; some of the data are given below.

A number of conclusions may be drawn from Fig. 30. As to dehydrating efficiency, it is apparent that $CuSO_4$, put in a moist atmosphere or into a non-reacting liquid containing water, will never remove all the water, but will combine with it at a given temperature *D* and reduce the aqueous pressure to a certain definite amount, depending on the quantity of $CuSO_4$ present; if it be so small that it is completely converted into $CuSO_4.5H_2O$, the pressure will fall to *G*; if it be larger, so that all the water possible can be taken up without the formation of any hydrate higher than $CuSO_4.H_2O$, the pressure will fall to *E*; but under no circumstances can it fall to zero. The same reasoning applies of course if other salts forming hydrates are used as desiccating agents. Further, it will be seen that, at a given temperature, all three hydrates are perfectly stable and capable of existence; there is no necessary lower limit for the existence of a hydrate in equilibrium with a vapor, although there frequently is a lower

TABLE XXX

DISSOCIATION PRESSURES OF HYDRATES OF COPPER SULFATE [1]

Temp.	$CuSO_4.5H_2O$ – $CuSO_4.3H_2O$	$CuSO_4.3H_2O$ – $CuSO_4.H_2O$	$CuSO_4.H_2O$ – $CuSO_4$
25°.....	7.8 mm.	5.6 mm.	0.8 mm.
30	11.6	—	—
35	16.5	11.8	—
40	23.2	—	—
45	32.8	22.1	—
50	45.4	30.9	4.5
80	260.1	183.1	—

[1] Chiefly from Carpenter and Jette, *J. Am. Chem. Soc.*, **45**, 578 (1923). See also Wilson, *ibid.*, **43**, 704 (1921); Noyes and Westbrook, *ibid.*, **43**, 726 (1921).

limit for its existence in contact with solution. The upper limit of a vapor-pressure curve of this character is reached where there is a congruent melting point or a transition, producing a liquid phase and therefore a new system with a new vapor-pressure curve. That this is the single limitation to the curves at high temperatures is frequently forgotten, and was not at all understood previous to the use of the phase rule; as a result, the student should be on his guard against statements emanating from the older literature to the effect that such and such a hydrate "loses water at 100°," when all that is meant is that the experimenter noticed a rapid loss of water at that temperature, and not that a transition point exists. As Fig. 30 indicates, a given hydrate will lose water at any temperature, if the aqueous pressure is less than that of its dissociation curve; in the terms of the phase rule, since a hydrate and its vapor constitute a bivariant system, they may exist at any pressure, if the temperature is low enough, and at any temperature if the pressure is high enough (provided only that a transition or melting point does not intervene).

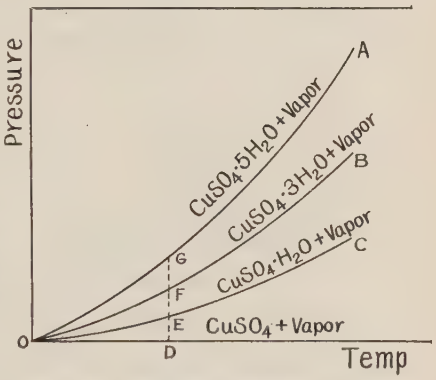


FIG. 30. Vapor Pressure Curves for Hydrates of Copper Sulfate

A pressure-composition diagram of the same system, given in Fig. 31, shows the conditions at a fixed temperature, taken arbitrarily here as 50° C. If anhydrous copper sulphate be introduced into a vessel and water vapor introduced continuously, the pressure will rise continuously along *ab* from zero pressure to 4.5 mm. before any water is taken up by the salt, since up to *b* the aqueous pressure is less than the dissociation pressure of the mono-

hydrate. At *b* the monohydrate begins to form, and since there are now two solid phases and vapor present at constant temperature the system is invariant and pressure increase is impossible as long as the three phases coexist. The water vapor continuously introduced is taken up in the formation of the monohydrate, resulting in a change of total composition of the solid phases along the line *bc*; when the conversion of $CuSO_4$ into $CuSO_4 . H_2O$ is complete, at *c*, the pressure again rises without affecting the composition of the monohydrate, along *cd*, until the dissociation pressure of the trihydrate is reached at *d* (30 mm.), at which point the trihydrate begins to form. Similar changes in direction of the vapor-pressure curve occur at *e*, *f*, and *g*; the diagram as a whole shows a series of horizontal curves where two solids and vapor are present.

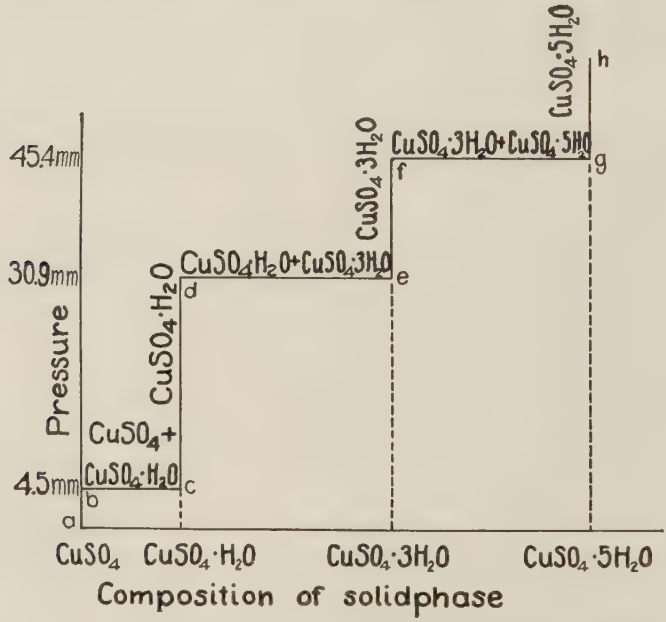


Fig. 31. The System, Copper Sulfate Water. Isotherm at 50° C.

The same general conditions, described above for systems in which a hydrate is formed, are met with in any system in which the two components form a solid compound or compounds, and a vapor composed of one component. Important examples which have been studied include among others the following systems: $CaO - CO_2$;[1] $AgCl - NH_3$,[2] and similar amines; $Hg - O_2$.[3] Systems in which both components are volatile, as in the case of $NH_3 + HCl$ and $NH_3 + CO_2$, exhibit more complicated relations.

The systems discussed or mentioned are characterized by the fact that the solid phases are either pure components or compounds, that is, they are phases

[1] Debray, *Compt. rend.*, **64**, 603 (1867); Le Chatelier, *ibid.*, **102**, 1243 (1883); Riesenfeld, *J. chim. phys.*, **7**, 561 (1909); Zavrieff, *ibid.*, **7**, 31 (1909); Johnston, *J. Am. Chem. Soc.*, **32**, 938 (1910); Jolibois and Bouvier, *Compt. rend.*, **172**, 1182 (1921). Smyth and Adams, *J. Am. Chem. Soc.*, **45**, 1167 (1923).

[2] Isambert, *Compt. rend.*, **66**, 1259 (1888).

[3] Pelabon, *Compt. rend.*, **128**, 825 (1899).

of fixed composition. If, however, the vapor phase is taken up by the solid to form a solid solution, a phase of variable composition results and the vapor-pressure curve obtained is quite different from those previously shown. In such a case the pressure-composition diagram is that of Fig. 32, in contrast with that of Fig. 31; as vapor is added, it goes partially into the solid phase to form solid solution, and, since two phases only are present, the curve *ab* results, indicating that the composition of the solid phase is altering with the pressure. If at some pressure *b* a compound forms, there are now three phases present and the system is isothermally invariant, as shown by the curve *bc*. It should also be pointed out that if, at *b*, a *second* solid solution forms, instead of a compound, the curve will take the same direction *bc* since the same number of phases is present. In short, though an ascending curve *ab* of Fig. 32 is proof that a phase of variable composition (solid solution) is being formed and a perpendicular (*ab* of Fig. 31) is proof that there is but one solid phase and of fixed composition present, a horizontal (*bc* of either Fig. 31 or 32) is proof of the existence of two solid phases, and does not distinguish between two compounds and two conjugate solid solutions. Interesting work has been done on systems in which gases form solid solutions, but not always with perfect success; as an example the adsorption of hydrogen by palladium, studied first by Graham and by a host of others,[1] has demonstrated that at least one solid solution is found, but whether there is also compound formation or the formation of a second solid solution is still an open question. Other cases however have yielded more satisfactory results; thus certain "hydrated" silicates and zeolites [2] have been shown to consist of solid solutions of water in the mineral, since they yield a sloping vapor-pressure curve with change of composition (*ab* in Fig. 32), and van Bemmelin [3] has shown, by similar evidence, that various supposed hydroxides, such as $Fe(OH)_3$, $Sn(OH)_4$, $Si(OH)_4$, $Cr(OH)_3$ and probably $Al(OH)_3$, are not compounds but, on the contrary, solid solutions of water in the various oxides. In accordance with this finding, it is proper to speak of these substances as hydrous oxides rather than hydroxides or hydrated oxides, since these latter terms imply definite composition.

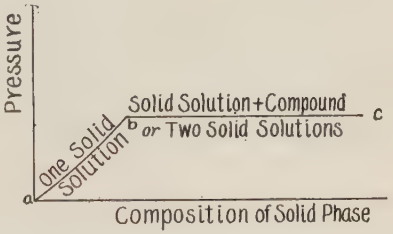


FIG. 32. Isotherm of System Forming Solid Solutions

E. The Equilibrium Solid-Solid

A type of solid-solid equilibrium which has been referred to only incidentally in the preceding treatment is the equilibrium between two conjugate solid

[1] See Gillespie and Hall, *J. Am. Chem. Soc.*, **48**, 1207 (1926).

[2] Tammann, *Wied. Ann.*, **63**, 16 (1897); *Z. physik. Chem.*, **27**, 323 (1899).

[3] van Bemmelin, *Ber.*, **11**, 2232 (1878); *ibid.*, **13**, 1466 (1880); *Rec. trav. chim.*, **7**, 37, 87, 106, 114 (1888); *J. prakt. Chim.*, (2) **46**, 497 (1892); *Z. anorg. Chem.*, **13**, 233 (1896).

solutions (curves *fe* and *gd* or *gb* in Figs. 24 and 25). It is obvious that such an area of conjugate solutions need not necessarily continue far enough toward higher temperatures to meet the melting-point curves, but may have its consolute point in the solid area just as conjugate liquids may have their consolute point in the liquid area (Fig. 11). The study of such conjugate solid solutions is naturally of great importance in metallography, since phase reactions occurring in the solids must have their effect upon the structure and physical properties of alloys. In general, the establishment of equilibrium between two solid solutions is slow, and is slower at lower temperatures than at higher. The process of annealing solid alloys, i.e., leaving them for long periods at as high temperatures as possible, has the purpose of facilitating the phase reactions, while the process of chilling is resorted to when it is desired to obtain a phase complex which is stable only at high temperatures but which if brought suddenly to low temperatures will remain in metastable equilibrium with changes so slow as to be negligible. The methods by which the phase relations of solid alloys are studied are necessarily much more difficult than those for liquid systems, and may be found described in the texts on metallography; the commonest methods are thermal in character (i.e., use of cooling curves and warming curves) or microscopical. Details as to solid systems cannot be given here, but a brief outline of some of the work on a single such system (the iron-carbon system, important because of the use of such alloys as steel) will be given in order to illustrate equilibria of this class.

When iron and carbon (the latter in any reasonably small proportion) are considered, the system is found to give rise to a very considerable number of solid phases, which may enter into various phase equilibria with each other or with the liquid solution of carbon in iron. Leaving the specific properties of these solid phases to be studied elsewhere, if the reader wishes, an enumeration of these solid phases is given below:

Three (possibly four) allotropic modifications of iron { α-ferrite, [β-ferrite], γ-ferrite, δ-ferrite

A carbide of iron, Fe_3C = Cementite

Solid solution of carbon in γ-ferrite = Austenite

Solid solution of carbon in δ-ferrite = ?

Two allotropic forms of carbon { graphite, amorphous carbon

The relationships of these phases have been extensively studied and are embodied in a voluminous literature. There is not an agreement on all of the details, because of the difficulty of the experimental work, but that on which there is common agreement [1] is diagrammed in Fig. 33. Leaving out of consideration the small area near *A* in which solid solution of carbon in δ-ferrite is found, the principal relationships will be mentioned. γ-ferrite dissolves carbon, giving rise to a solid solution called Austenite, occupying the field *AEHGF*. The

[1] See Desch, Metallography, 1922, p. 363. Longmans, Green and Co.

dissolving of carbon in the iron brings a fall in the melting point, giving rise to a liquidus curve (*AC*) and a solidus curve (*AE*) such as always occur when solid solution is formed. These curves fall in this case to a eutectic *C*, as previously shown in Fig. 24; the three phases are a liquid and two conjugate solids, Austenite (*E*) and the carbide of iron Fe_3C known as Cementite (*D*); the eutectic temperature is 1130° C., and the composition is 4.3 per cent carbon. There is of course a second area of conjugate liquid-solid phases, *CBD*, where the solid phase is Cementite. If we now follow the curves of the conjugate solids, *EH* and *DL*, an interruption occurs at the point *H*, where the curve for Austenite (*EH*) meets the curve for the transition of γ-ferrite into α-ferrite (*FGH*). Regarding β-ferrite and α-ferrite as identical except for the occurrence of magnetic properties in the β-ferrite, or adopting any of the other views which have been advanced [1] to the effect that the two

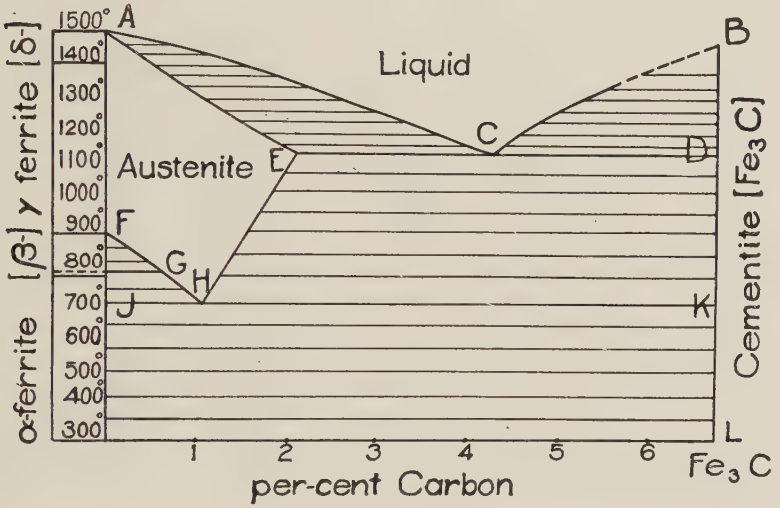


Fig. 33. The System, Iron-Carbon

varieties are not allotropic forms, we may look on the point *F* (900°) as the transition point of pure γ-ferrite into pure α-ferrite, and *FGH* as the curve showing the depression of this transition point by the presence of carbon dissolved in the one solid (Austenite). The intersection of these two curves at *H* (0.89 per cent *C* and 700°) gives a point of equilibrium of three solid phases, namely, α-ferrite, Austenite, and Cementite, and is called a eutectoid; it resembles a eutectic in being the point of equilibrium between two components (here α-ferrite and Cementite) and a solution (here Austenite), differing from the eutectic in that the solution is here a solid solution in place of a liquid solution. At temperatures below the eutectoid there will be two solid phases in equilibrium, namely, α-ferrite and Cementite; these will settle out on cooling in the usual form of a eutectic conglomerate, which, because of its approximation to homogeneity, is looked upon as a structural element and called Pearlite.

By drawing isopleths at the different compositions, it will be easy to see what changes occur when the liquid mass is cooled. Any deductions thus made however are upon the assumption that these various equilibria are attained, and of course metastable conditions may easily persist, particularly

[1] See Desch, p. 366, for references.

if the cooling is rapid. Indeed it has been advanced [1] that all the equilibria here represented are metastable, and that the true equilibrium is one between the two solid phases ferrite and graphite. While the study of the iron-carbon systems from the standpoint of the phase rule is by no means yet complete, it has nevertheless been of very great value in making plain a number of the relationships.

Systems of Three Components

In passing to systems of three components, brief study of the new relations of components, variables and degrees of freedom will be helpful. With respect to components, no new principle is involved, but it will be useful to note what general types of reacting substances fall under the heading of ternary systems. Perhaps the most frequently studied cases are those consisting of water with two salts having a common ion, such as $NaCl + KCl + H_2O$; such a system, if it includes new compounds, can have them only of a composition intermediate between that of two or more components, such as double salts or hydrates, and therefore any phase which occurs can have its composition expressed in terms of the three components. It will be noted that a system consisting of water and two salts without a common ion would not fall into the division of ternary systems, since by double decomposition new phases may be produced whose composition is not intermediate between the two salts and water; this very common type of system is a four-component system. On the other hand, two salts without common ion do form a ternary system if water or other substances be absent; although the chemical equation for the double decomposition shows four compounds present, yet any one of them can have its composition expressed in terms of the other three, as was discussed earlier for the reaction

$$CaCO_3 \rightleftharpoons CaO + CO_2,$$

where the system was shown to be binary despite the existence of three compounds. A third common instance of a ternary system consists of a single salt and water where the salt suffers hydrolysis, forming basic or acidic salts whose composition again is not intermediate between the salt and water; in this case, the choice of the three components depends upon convenience in representing the system, and an excellent example exists in the case of bismuth nitrate and water, which is most conveniently regarded as having the three components Bi_2O_3, N_2O_5 and H_2O.

The number of independent variables in a ternary system is larger by one than for a binary system, namely, pressure, temperature and two concentration variables, since a ternary solution requires a statement of its composition with respect to two components before its total composition is fixed. The degrees of variance for ternary systems follow directly from substitution in the phase-

[1] Charpy and Grenet, *Bull. Soc. d'Encouragement*, 1902, 399.

rule equation; five coexisting phases at a quintuple point give an invariant system, four give a univariant system, three a bivariant and so on.

In dealing with three-component systems, a complete treatment must include equilibria in which the vapor phase is included as well as those involving liquid and solid phases. We shall confine ourselves here, however, toc ondensed systems, in which the gaseous phase is not present. With respect to gaseous equilibria it will only be stated that various types of curves are obtained to represent the boiling points, as in binary solutions, and that three-component azeotropic solutions are also met with; these latter are sometimes of considerable value in making possible the removal of one component of a binary mixture which cannot be separated by fractionation of that mixture. Details of such cases may be found in Young's [1] book.

Graphic Representation of Ternary Systems: Complete representation of all the variables in ternary systems is a complex matter, if at all possible. In most work that has been accomplished such a representation is unnecessary, since the systems studied have been chiefly condensed systems in which the pressure has been kept constant or is ignored. Our problem is therefore to represent the temperature as one variable and the composition as a second. Many geometrical means have been devised for this purpose, of which only one will be discussed and used here, namely, the representation of the composition by triangular coördinates and of the temperature at right angles to the triangular diagram, giving, therefore, a triangular prism as the space figure in which the two variables are represented. At any fixed temperature, the isotherm would then be a triangle, representing the composition, the properties of which will be briefly discussed.

Following the method of Gibbs,[2] an equilateral triangle is chosen and the composition of each pure component represented by a vertex (*A*, *B* and *C* in Fig. 34); the total or unit composition is expressed by the altitude of the triangle, and the fractional part which a particular component contributes to a complex is measured by the perpendicular distance of the point representing that complex from the side opposite the vertex for that component. Thus the point *m* represents a complex made up of component *A* in amount proportional to the perpendicular *ma*, *B* in the proportion *mb*, and *C* in the proportion *mc*, a representation made possible by the property of an equilateral triangle that the sum of the perpendiculars from a point to the three sides is equal to the altitude of the triangle. For the general properties of the equilateral triangle the reader is referred elsewhere; yet one such property is of such usefulness to our problem as to warrant explicit statement, namely, that if a complex of *A* and *C* represented by the point *x* is taken and increasing amounts of *B* added, the composition will change along the straight line *xB* and therefore all points on such a straight line represent the same ratio of *A* and *C* to each other.

The discussion of ternary systems must necessarily be abbreviated; a few

[1] Sidney Young, Distillation Principles and Processes, Macmillan and Co., London, 1922.

[2] Gibbs, *Trans. Conn. Acad.*, **3**, 176 (1876); Stokes, *Proc. Roy. Soc.*, **49**, 174 (1891); Roozeboom, *Z. physik. Chem.*, **15**, 984 (1894).

only of the many possible relationships will be shown under the three following headings.

Systems Consisting of Liquid Phases Only: Since any liquids may be solidified or vaporized by suitable temperature changes, it is obvious that we can speak of a ternary system as consisting exclusively of liquids only if the temperature is stated, or in other words, that we are discussing only certain isotherms

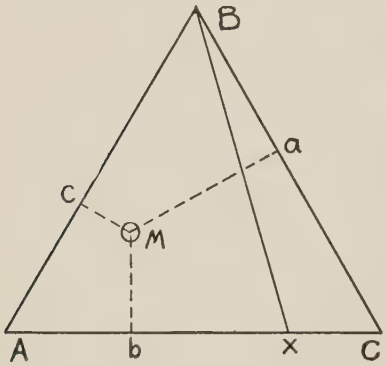


Fig. 34. Equilateral Triangle for Composition of a Ternary System

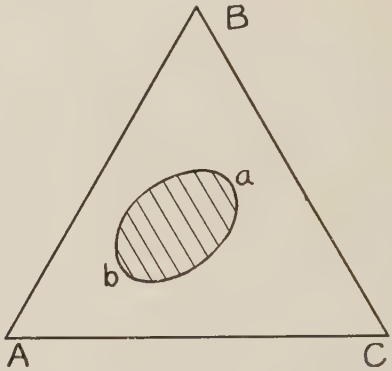


Fig. 35. Ternary System with a Single Binodal Curve

of a system which will show solid phases at certain lower temperatures. The three liquids taken for study (A, B and C of Fig. 35) are best considered as making up three pairs, $A + B$, $A + C$ and $B + C$; indeed, our ternary systems in general are to be considered as composed of the three binary systems. If each of the three pairs shows unlimited mutual solubility, it usually follows that any ternary mixture also will give a single liquid phase; but this is not universally so, and instances are known in which, within certain limits of concentration, the system separates into two conjugate liquid layers, shown schematically in Fig. 35 by the closed curve *ab*. Within this closed curve tie-lines have been drawn connecting the two conjugate liquids, and any complex taken within that area will separate into two liquid phases represented by the ends of the tie-lines. Such a closed curve has been found for the system water-phenol-acetone [1] at temperatures above 68°, at which all three pairs of components are completely soluble, and has also been found in a few other cases.[2] The boundary curve for this two-liquid area is called a binodal curve, and the interesting character of the points *a* and *b* will shortly be seen.

A single binodal curve is much more often met with where one of the three binary systems shows limited solubility of the liquids. Such a case is that of chloroform, water, and acetic acid (Fig. 36) in which the two components chloroform and water have a limited solubility, giving rise to the two conjugate

[1] Schreinemakers, *Z. physik. Chem.*, **33**, 84 (1900).

[2] Hill, *J. Am. Chem. Soc.*, **44**, 1186 (1922); Hill and Miller, *ibid.*, (1924).

solutions a and b. As acetic acid is added to these two liquids it distributes itself between the two phases in unequal amounts and also brings about an increase in the mutual solubility of chloroform and water; any particular tieline, such as $a'b'$, is therefore not parallel to the base of the triangle. Increasing additions of the acetic acid bring the two conjugate liquids nearer and nearer toward each other in composition, until at k they become identical; k is therefore a critical point, although it is more commonly spoken of as the plaitpoint, and the binodal curve is accordingly a distribution curve of acetic acid in water and chloroform. The figures for the 18° isotherm are given opposite.

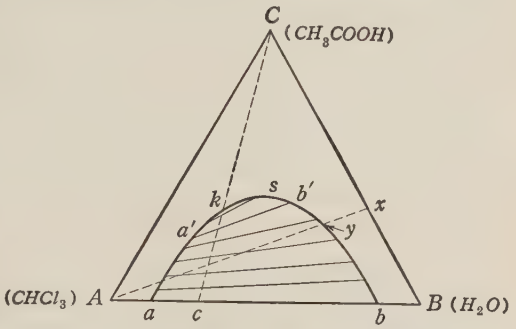


FIG. 36. The System, Chloroform-Water-Acetic Acid, (Schematic)

Distribution curves such as the foregoing have many points of general interest. It will be noted that the distribution ratio of the acid between the two phases is by no means a constant, but varies as the acid brings about changes in the mutual solubility of the chloro-

TABLE XXXI

$CHCl_3$ — H_2O — CH_3COOH AT 18° [1]

Heavy Phase			Light Phase		
$CHCl_3$	H_2O	CH_3COOH	$CHCl_3$	H_2O	CH_3COOH
99.01	0.99	0	0.84	99.16	0
91.85	1.38	6.77	1.21	73.69	25.10
80.00	2.28	17.72	7.30	48.58	44.12
70.13	4.12	25.75	15.11	34.71	50.18
67.15	5.20	27.65	18.33	31.11	50.56
59.99	7.93	32.08	25.20	25.39	49.41
55.81	9.58	34.61	28.85	23.28	47.87

[1] Wright, *Proc. Roy. Soc.*, **49**, 174 (1891); *ibid.*, **50**, 575 (1892).

form and water, as was discussed in the section on the distribution law; a distribution curve which followed the law exactly would be shown by two straight lines running from a to C and from b to C, and in practice no such curves have been found. Again, the plait-point k is almost always found to one side or the other of the maximum point of the curve, S, and therefore is not at the point of the maximum solubility of A and B in each other. If one adds the component C to A and B, the system will pass through the critical point k only if the initial composition is on the line Ckc; any other initial composition will, on addition of C, lead to the disappearance of one phase at the expense of the other rather than in the reaching of the critical state, just as was shown for two-component systems in Fig. 11, where the critical state was reached by change of temperature instead of change of composition at a fixed temperature as in Fig. 36. Other excellent examples of liquid systems showing a

single binodal curve are the systems silver-lead-zinc,[1] in which the desilverization of lead is accomplished by the use of molten zinc (Parkes's process), and the system water-toluene-acetone.[2] Such a diagram as Fig. 36, if carefully drawn to scale, gives an accurate method for analysis of a solution of the components B and C, which are otherwise not easily determined if they are organi substances; to the solution of unknown composition, x, the third component A is added from a burette up to the point where the first appearance of a turbidity indicates that the binodal curve (akb) has been reached; the outline of the curve being accurately known, the point where it crosses the line corresponding to the amount of A added (y) is taken, and it follows that the original composition x is on the straight line Ayx.

It is clear from the diagram (Fig. 36) that any complex taken outside of the two-liquid area akb will give a single liquid phase; such a system (liquid + vapor, with temperature fixed) is bivariant, and the composition may be altered with respect to any two of the three components, within the limits of the bivariant area.

Where ternary systems are taken, of which two of the binary systems show limited solubility, two binodal curves are obtained, as in Fig. 37; the diagram offers no points different from those previously discussed. There are, however, some interesting results that follow if the temperature is altered, since the two binodal curves may, generally speaking, be made to expand either by increase or decrease of temperature until they meet. If the juncture at some different temperature occurs at the two plait-points, k and k', the two curves merge into

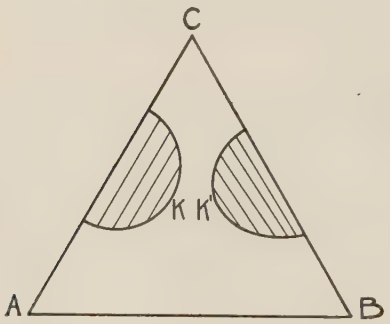


Fig. 37. Ternary System with Two Separate Binodal Curves

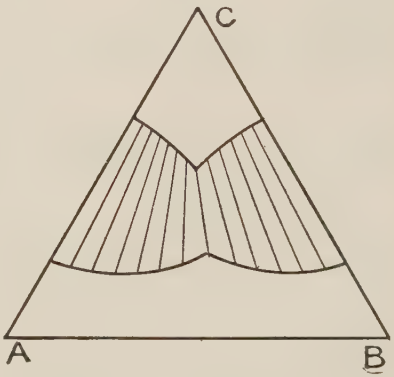


Fig. 38. Ternary System with Two Binodal Curves, Joined at Plait-points

each other to form a continuous band (Fig. 38). Water, phenol and aniline[3] show this condition at temperatures in the neighborhood of 50°. If, on the other hand, the two curves meet in such fashion that the two plait-points do not come in contact, the system shows an area in which three liquid phases are coexistent (abc of Fig. 39). This interesting occurrence,[4] found for the systems silver perchlorate-benzene-water and silver perchlorate-toluene-water, may be explained by noting that the solution a on the binodal curve which has its base

[1] Bodländer, *Berg- und Huttenmänn. Ztg.*, **56**, 331 (1897).
[2] Walton and Jenkins, *J. Am. Chem. Soc.*, **45**, 2555 (1923).
[3] Schreinemakers, *Z. physik. Chem.*, **29**, 586 (1899).
[4] Hill, *J. Am. Chem. Soc.*, **44**, 1163 (1922); Hill and Miller, *ibid.*, **47**, 2702 (1925).

on AC, must of course have a solution b of the same curve conjugate with it; by like reasoning, since a is also on the other binodal curve, there must be a solution c conjugate with it on the same binodal curve. The two curves, however, do not of necessity have their tie-lines parallel at the point of their juncture, and therefore b and c are not the same point; but, since they represent solutions in equilibrium with the same solution a, they must be also in equilibrium with each other, giving rise to a tie-line bc. There is now a triangular area abc representing three liquids and vapor in equilibrium at a fixed temperature; with these five restrictions the system is by rule invariant, or better said, isothermally invariant, and any complex taken within the area abc will separate into three coexistent liquid phases of the composition indicated by a, b, and c.

If ternary systems are sought, in which each of the three binary systems shows only partial miscibility, examples will not so readily occur to mind. As a matter of fact, however, some twelve or more cases have been noted and given more or less study; most interesting are the ternary alloy iron-zinc-lead [1] and the system succinic nitrile-water-ether,[2] which latter Schreinemakers has studied exhaustively. In such instances, a three-liquid area such as is shown in Fig. 40 is sure to occur if the three binodal curves can be brought to meet each other by raising or lowering the temperature.

In the foregoing treatment a series of arbitrarily chosen isothermal sections has been discussed. It will be seen that if a series of such sections for any system be placed in regular order, they would produce a triangular prism, and the binodal curves represented in Figs. 36 to 40 would form the boundary surfaces of loaf-shaped volumes representing the concentration and temper-

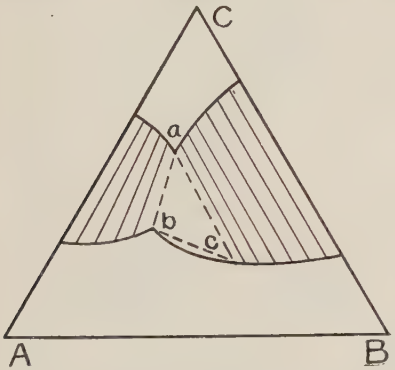


Fig. 39. Ternary System with Two Binodal Curves, Showing Three Liquid Phases

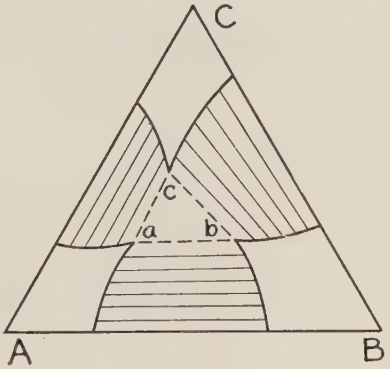


Fig. 40. Ternary System with Three Binodal Curves

ature limits of the conjugate solutions. A line on such a surface joining the plait-points k at the different temperatures would be a critical curve, terminating at the point C of Fig. 11, on one of the binary surfaces. Such a line might,

[1] Timmermanns, *Z. physik. Chem.*, **58**, 159 (1907).

[2] *Z. physik. Chem.*, **25**, 545 (1898).

however, have its point of maximum temperature at a temperature beyond the terminal point C of Fig. 11; in that case the maximum point would be in the interior of the prism, and is called a ternary critical point. The development of ternary systems with respect to the temperature axis will be taken up in greater detail in the following section.

Systems Consisting of Solid Phases, With a Single Liquid Phase: In order to visualize the relations that exist in ternary systems when solid phases are present, let us assume that we are dealing with three solid components at some temperature sufficiently below their melting points so that they do not have any effect upon each other; and let us also assume that the solids show no tendency to form solid solutions. If such a mixture of the three solids is

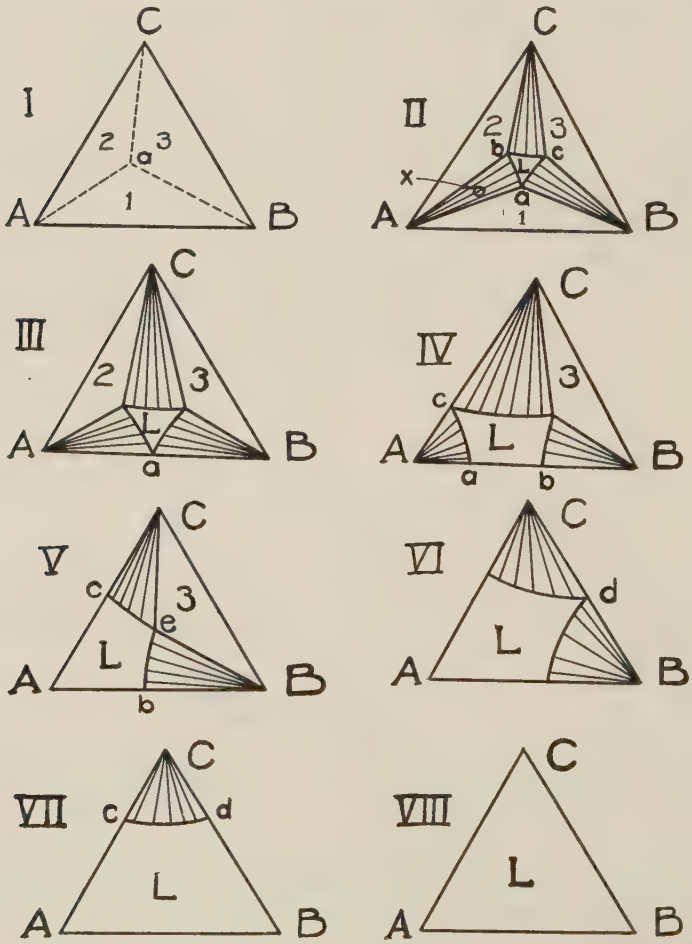


FIG. 41. Ternary Systems, with a Single Liquid Area

subjected to a rising temperature, it will go through a series of changes which have been shown schematically in Fig. 41.

At some temperature a liquid phase will appear, of a composition represented by *a* in sketch I; this will be the temperature at which the three solids, the new liquid phase and the vapor are coexistent, and is therefore a quintuple point and of course invariant; it is spoken of as the ternary eutectic point for the system. If now the temperature rises further, the composition area in which the liquid can exist spreads to some such form as is marked *L* in sketch II. At this higher temperature we can no longer have all three solids in contact with the liquid, since we are above the quintuple point, but a number of different equilibria or phase complexes come into existence, as shown in the diagram. Any complex taken within the area *abc* will give only a liquid and its vapor, and is therefore isothermally bivariant. Any complex *x* taken within the triangle *Aab* will give solid *A* and a liquid phase of that composition on the line *ab* at which the tie-line from *Ax* passes through *ab*; the system, consisting of solid, liquid and vapor, is isothermally univariant, and if any change in the amount of either *B* or *C* is made, the composition of the liquid phase which forms is at once fixed, as shown by the tie-lines. The same discussion applies to the two other triangles *Bac* and *Ccb*. Finally there are present three triangular areas marked 1, 2 and 3; these represent isothermally invariant areas, within which any total complex will change into two solids and a liquid, as represented by the vertices of the triangles, together of course with vapor.

As the temperature is raised further, the system goes through a variety of changes (III to VIII) which reduce the number of equilibria one by one. In III the point *a* has moved until it touches the base-line *AB*; this is a temperature at which a binary liquid composed of *A* and *B* is in equilibrium with the two solid components, and will be recognized at once as the eutectic for the binary system *AB* (point *C*, Fig. 14). In sketch IV, the liquid has reached the binary eutectic for *A* and *C* at the point *c*. This extension of the liquid area *L* has, it will be seen, terminated successively the invariant equilibria 1 and 2. At higher temperatures the liquid area has spread along *AB* (sketch IV) and this movement is describing the two solubility curves on the binary surface *AB* (lines *CR* and *CM* of Fig. 14). In sketch V the point *a* has reached the freezing point of *A*, and the equilibrium of solid *A*, liquid and vapor shown as *Aac* in sketch IV has disappeared. Sketch VI shows the liquid area reaching the binary eutectic for *B* and *C* at *d*, terminating the invariant equilibrium 3, and sketch VII shows that the freezing point of *B* has been reached. With increasing temperature the solubility curve *cd* rises until, when the freezing point of *C* has been reached in sketch VIII, the system will give a liquid phase whatever composition is taken. It will be seen that the fixed temperatures in such a system consist of a single quintuple point (the ternary eutectic), of three binary eutectics and three freezing points of components.

Some of our best known ternary systems have isotherms like those shown in Fig. 41. Thus, for example, Schreinemakers [1] found that the 30° isotherm for the system $(NH_4)_2SO_4$-NH_4Cl-H_2O is exactly like sketch V, where *A* stands for H_2O, *B* for NH_4Cl and *C* for $(NH_4)_2SO_4$; the solution *e*, saturated with respect to both salts, contains 17.6 per cent of NH_4Cl and 25.7 per cent of $(NH_4)_2SO_4$, while *b*, saturated with NH_4Cl alone, contains 29.5 per cent of that salt and *c* contains 44 per cent of $(NH_4)_2SO_4$. Such a diagram (V) will in general express the relations of two salts with a common ion in water at laboratory temperature, which is above the melting point of ice, above the eutectics for water with each of the salts, and, of course, below the eutectic for the two salts alone.

A simple extension of the diagrams of Fig. 41 will suffice for cases where two components form a compound, called a binary compound, or where all three unite to form a ternary compound. The composition of any binary compound will be expressed by a point on one of the sides of the triangle, while that of a ternary compound will fall within the triangle.

[1] *Z. physik. Chem.*, **69**, 557 (1909).

The interesting system of bismuth nitrate and water will afford an example showing ternary compounds; as previously explained, this is a three-component system, and is diagrammed with Bi_2O_3, N_2O_5 and water as the three components. Fig. 42 shows schematically the relationships as found by Rutten and van Bemmelin [1] for 20°. The system at this temperature shows four ternary compounds which are marked I, II, III and IV in the figure. The composition of each is given below.

Point in Fig. 42	Composition	Conventional Formula
I	$Bi_2O_3.N_2O_5.2H_2O$	$BiONO_3.H_2O$ (basic salt hydrate)
II	$Bi_2O_3.N_2O_5.H_2O$	$Bi_2O(NO_3)_2(OH)_2$ (basic salt hydrate)
III	$Bi_2O_3.3N_2O_5.10H_2O$	$Bi(NO_3)_3.5H_2O$ (normal salt hydrate)
IV	$Bi_2O_3.3N_2O_5.3H_2O$	$Bi(NO_3)_3.1\frac{1}{2}H_2O$ (normal salt hydrate)

It will be seen that each of these solid phases may be in equilibrium with solutions varying in composition over a limited range (*ab*, *bc*, *cd*, *de*) and that two solid phases can be in equilibrium only with a solution of fixed composition, as shown by the triangles having *b*, *c*, and *d* as their angles.

With these several types of isotherms before us, it will not be difficult to construct a picture of the triangular prism that will show the temperature as a variable, and of which the isotherms studied are simply cross-sections. Fig. 43 shows such a diagram. The point *d* is the ternary eutectic, or quintuple point, below which all mixtures of the components can exist only in the solid state. The points *a*, *b* and *c* are the three binary eutectics for the three two-component systems, and *e*, *f* and g are the melting points of the three components. The three shaded surfaces separate the region of solid phases below from the region of liquid

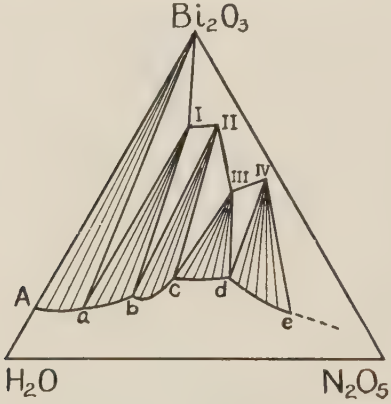


Fig. 42. The System Bi_2O_3 — N_2O_5 — H_2O (Schematic)

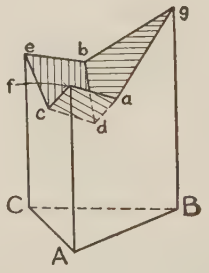


Fig. 43. Ternary System Showing Ternary Eutectic

phases above. These surfaces represent a single solid phase (*B* for *bgad*, etc.) in equilibrium with liquid, the lines *ad*, *bd* and *cd* represent two solid phases in equilibrium with liquid, and the point *d* represents the three solids with liquid. If then we consider any liquid of composition above the diagram as cooled down gradually, it will precipitate a single solid phase where the isopleth passes into one of the surfaces, and as the temperature continues to drop, the composition of the remaining liquid must begin to vary along this surface as more and more of the one component settles out, until a point is reached on one of the eutectic curves *ad*, *bd* or *cd*. Here a second solid will begin to precipitate and the composition and

[1] *Z. anorg. Chem.*, **30**, 342 (1902).

temperature of the solution will vary along the specific eutectic curve until finally, at *d*, the system becomes invariant (three solids, liquid and vapor) and no change in composition of the liquid occurs while it is solidifying completely. It is clear that a knowledge of such a complete diagram for a ternary alloy will enable the metallurgist to foretell in what order and fashion the three components will solidify from a given complex taken. Further, since the ternary eutectic is necessarily lower than all the binary eutectics, it becomes possible to contrive especial low melting alloys of three components; the following examples will illustrate the point.

TABLE XXXII

EUTECTICS IN TERNARY ALLOYS

Pb — Bi — Sn [1]			Pb — Bi — Cd [2]		
M.P. of Component	Binary Eutectic	Ternary Eutectic	M.P. of Component	Binary Eutectic	Ternary Eutectic
Pb = 325°	Pb + Bi = 127°	96°	Pb = 320°	Pb + Cd = 245°	92°
Bi = 268°	Bi + Sn = 133°		Cd = 320°	Cd + Bi = 145°	
Sn = 232°	Pb + Sn = 182°		Bi = 270°	Pb + Bi = 125°	

[1] Charpy, *Compt. rend.*, **126**, 1569 (1898).
[2] Bartow, *J. Am. Chem. Soc.*, **32**, 1410 (1910).

Systems With Several Solid Phases and Several Liquid Phases: It is possible now, with the information gained in the previous two sections, to discuss any isotherm of any condensed system without bringing in any relationships not already met with. Any isotherm will show only the following parts, which can all be found in Figures 35 to 42: binodal curves, solubility curves, and isothermally invariant triangles, which later may connect at their vertices three solids (Fig. 41, I, *ABC*), two solids and one liquid (Fig. 42, I, II, *b*), two liquids and one solid (shown later in Fig. 44, *Acd*), or three liquids (Fig. 40, *abc*). Of course, the number of such equilibria at a given temperature may be either small or large, and the possibilities of combinations are very many indeed and only a relatively small proportion of them have thus far been investigated. Two such cases will be shown here.

Fig. 44 shows a fairly common type of ternary isotherm occurring when two mutually soluble liquids *C* and *B* are treated with a single solid which is freely soluble in one of them and sparingly soluble in the second. Such a case will be more readily recognized if the usual laboratory method of preparing it is stated. If we have a saturated aqueous solution of some inorganic salt, such as potassium fluoride in water, and add alcohol to it, the alcohol at first passes into the liquid phase, but on continued addition finally gives rise to a second liquid phase; the mutual solubility of the two liquids in each other has been diminished by the presence of the salt. The triangle *Abd* represents the solid salt in equilibrium with solution consisting of water with more or less alcohol along the solubility curve *bd*, the triangle *Aac* in like fashion represents the salt in equilibrium with solutions chiefly alcoholic in content, and since the solubility of the salt in alcohol is usually small, the point *a* is close to *B* and the curve *ac* is short. The triangle *Acd* shows an isothermally invariant equilibrium of the two saturated solutions *c* and *d* in contact with solid salt *A*. The curve *ced* is a binodal curve for the two liquid phases that are in equilibrium with each other, as shown by the tie-

lines; and, finally, the area *BCbdeca* is the area for the bivariant solution, and shows the limits within which the three components will form a single liquid solution. Such systems as the above occur in the organic laboratory in the familiar operation of "salting out" one liquid from another by addition of a properly chosen salt; by addition of it to saturation, the complex will fall in the triangle *Acd*, and, since the solutions *c* and *d* cannot vary in composition at a fixed temperature, it is obvious that further addition of salt after solid phase appears is of no effect. In addition to numerous cases of the above type in which the isotherm is known qualitatively, a considerable number have been studied quantitatively; the work of Frankforter [1] and others gives excellent examples.

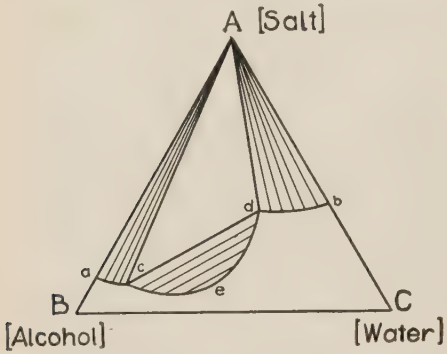


FIG. 44. The System, Alcohol-Water-Salt

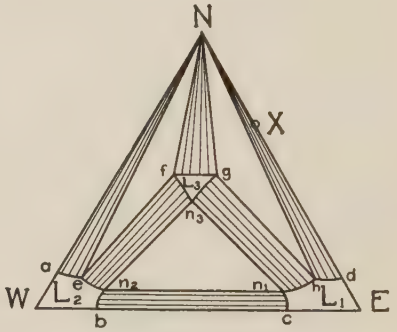


FIG. 45. The System Succinic Nitrile-Ether-Water (Schematic)

Fig. 45 represents no such familiar type of isotherm as the preceding, but is selected to show that a large number of equilibria frequently come into being in ternary systems. Schreinemakers [2] found for the system water-ether-succinic nitrile that twelve different equilibria or phase complexes exist at 2°, as shown in the figure and enumerated below:

3 areas for 1 liquid phase (marked L_1, L_2, L_3) = bivariant,
3 areas for 2 liquid phases (efn_3n_2, ghn_1n_3, cbn_2n_1) = univariant,
3 areas for 1 solid + 1 liquid (*Nae*, *Nfg*, *Nhd*) = univariant,
2 areas for 1 solid + 2 liquids (*Nfe*, *Ngh*) = invariant,
1 area for 3 liquids ($n_1n_2n_3$) = invariant.

It will appear that in such a system as this, if one took an amount of nitrile and ether represented by the point *X* and added water to it at this temperature, the changes will be those shown on a line running from *X* to *W*; there will be seven entirely different complexes obtained by the formation and disappearance of phases, which the student can tabulate by comparing the list of phases present in the first area *Nhd* with those found in each area crossed successively by the line.

Space does not permit a discussion of the complete diagrams that have been worked out to show the effect of changing temperature upon complex ternary systems such as the foregoing. It will be apparent, however, that where the

[1] Frankforter and Frary, *J. Phys. Chem.*, **17**, 402 (1913). Frankforter and Bell, *J. Am. Chem. Soc.*, **36**, 1103 (1914).

[2] *Z. physik. Chem.*, **25**, 543 (1898).

coexistence of three liquid phases is possible and where there are three solids possible (or more if binary or ternary compounds exist) as well as a vapor, a considerable number of quintuple points may be looked for at which five phases are coexistent. The ternary eutectic shown in Fig. 43 is by no means the only point of fixed temperature found in ternary systems; wherever five phases are found to coexist, the temperature will remain perfectly stationary upon addition or subtraction of heat until one of the phases disappears. Where complete studies of ternary systems like that of Fig. 45 have been made, a considerable number of these fixed points have been met with; thus, the system silver perchlorate-water-benzene [1] shows six quintuple points, ranging from $-58.4°$ to $+42.1°$, and eighteen monovariant equilibria.

Many interesting examples of condensed ternary systems have been studied in detail; the system potassium chloride-magnesium chloride-water was investigated by van't Hoff and Meyerhoffer [2] as part of an extremely valuable research on the Stassfurt salt deposits; the system ferric chloride-hydrogen chloride-water [3] is of interest in showing the effect of the acid upon the concentrations in which the various hydrates of ferric chloride can exist. In addition to studies of condensed systems such as the foregoing, there has been much valuable work on ternary systems in which liquid phases are absent; the study of the system iron-carbon monoxide-carbon dioxide [4] has given much useful information relative to the types of reaction occurring in the blast furnace and in hydrogen manufacture.

Indirect Analysis of Solid Phases: In the discussion of binary systems, it was pointed out that direct analysis of solid phases is beset with difficulties, and that it is usually necessary to resort to indirect analysis, thermal methods being the simplest. In condensed ternary systems thermal analysis is also possible, but it happens that other methods are available which are much simpler in execution—indeed, much simpler than for binary systems. Bancroft [5] has given the simplest exposition of this method, although it has also been proposed by Schreinemakers and others. In Fig. 46 let *ab* be a portion of a solubility curve, and the problem be to determine whether the solid phase is pure *B*, some compound of *A* and *B*, or a ternary compound of *A*, *B* and *C*.

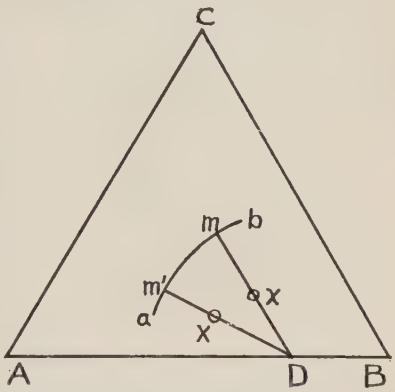


Fig. 46. Indirect Analysis for Solid Phase in a Ternary System

Let a complex *x* be made up by weight, brought to equilibrium with its saturated solution and the composition of the solution found by analysis to be *m*; then, as pointed out for other isothermally univariant equilibria, the tie-line *mx* and its prolongation must connect the

[1] Hill, *J. Am. Chem. Soc.*, **44**, 1169 (1922).

[2] *Z. physik. Chem.*, **27**, 75 (1898); **30**, 86 (1899).

[3] Roozeboom and Schreinemakers, *Z. physik. Chem.*, **15**, 588 (1894).

[4] Baur and Glaessner, *Z. physik. Chem.*, **43**, 354 (1903). Chaudron, *Ann. Chim.*, **16**, 221 (1921). Eastman and Evans, *J. Am. Chem. Soc.*, **46**, 888 (1924).

[5] *J. Phys. Chem.*, **6**, 178 (1902).

compositions of the liquid phase and the solid phase, and the solid must therefore lie somewhere along mx. Let the experiment be repeated with a second complex x' giving a solution m'; by the same reasoning the solid falls upon the prolongation of the tie-line $m'x'$. The only composition fulfilling both these requirements is that shown by the intersection of the two lines, here shown as D, and indicating that the solid phase is a binary compound of A and B and of the composition D. If the solid phase were the pure component B, the two tie-lines would intersect at B; if it were a ternary compound, they would intersect within the triangle, and if it were a solid solution of A and B, they would intersect at some point outside the triangle. The trial with a third tie line would distinguish between a ternary compound, where all lines would intersect at a point within the triangle, and on the other hand a ternary solid solution, shown by the failure of the lines to intersect at a single point; the three intersections, however, would fall within the triangle. The method is as simple in its experimental execution as it is straightforward in its logic.

Systems of Four and Five Components

For consideration of systems of more than three components, the reader is referred to the text-books on the phase rule. Work on systems of four or more components is necessarily more difficult than on simpler systems, and the graphical representation of results is necessarily more complicated; nevertheless, a considerable amount of valuable work has been done on such systems, including the study of a number of reciprocal salt pairs in water,[1] which is the convenient term for metathesis or double decomposition occurring in aqueous solution, and including such important technical reactions as the manufacture of potassium nitrate from sodium nitrate [2] and the ammonia process for manufacturing sodium bicarbonate.[3] Study of four-component systems and of systems of five and six components have made possible the commercial extraction of potash, chiefly as KCl, from the Stassfurt salts [4] in Germany and from the Searles Lake deposits [5] in this country.

THE THERMODYNAMICS OF HETEROGENEOUS EQUILIBRIA [6]

The position of equilibrium of a given process in one phase may be referred to that obtaining in another phase by application of the distribution law to the individual components of the process in the two phases. Consider the general case of a reaction proceeding in the vapor phase and simultaneously in the liquid condition. Let the reaction be generalized by the equation

$$aA + bB = cC + dD.$$

From the thermodynamic reasoning given in the preceding chapter the respective equilibria in the two phases are, in the gas phase

$$K_P = \frac{P_C{}^c \times P_D{}^d}{P_A{}^a \times P_B{}^b}$$

[1] Meyerhoffer and Saunders, *Z. physik. Chem.*, **28**, 453 (1899); **31**, 370 (1899).

[2] Uyeda, *Mem. Coll. Sci.*, Kyoto II, 245; Reinders, *Proc. K. Akad. Wetenschap. Amster.*, **16**, 1065 (1914).

[3] Fedotieff, *Z. physik. Chem.*, **49**, 162 (1904).

[4] van't Hoff, Zur Bildung der Ozeanischen Salzablagerungen, Braunschweig, 1905.

[5] Teeple, The Industrial Development of Searles Lake Brines, New York, 1929.

[6] Contributed by the Editor.

and in the liquid phase

$$K_X = \frac{X_C{}^c \times X_D{}^d}{X_A{}^a \times X_B{}^b},$$

where P and X refer to the respective partial pressures and mol. fractions. The relations between the various quantities in the two equations are connected by means of expressions, based upon the distribution law, of the form

$$P_A = k_1 X_A; \qquad P_B = k_2 X_B; \qquad P_C = k_3 X_C; \qquad P_D = k_4 X_D.$$

It therefore follows that

$$K_P = K_X \frac{k_3{}^c \times k_4{}^d}{k_1{}^a \times k_2{}^b}.$$

An example of this type has recently been studied by Edgar and Schuyler [1] in the esterification equilibrium. The equations given imply that the solution has the properties of a perfect solution. Where this does not hold the equations become more complex as outlined in the first section of this chapter.

The equilibrium, K_X', in one solvent can similarly be related to the equilibrium, K_X, in another solvent by means of the partition coefficients of the respective molecular species between the two solvents.

Gas-Solid Equilibria: In the case of heterogeneous reactions, for example, between gases and solids, a knowledge of the saturated vapor pressure of the solid constituents enables one to refer the reaction to that taking place in the homogeneous gas phase. A simple typical heterogeneous reaction may be used by way of illustration, the oxidation of sulphur to sulphur dioxide. This reaction may occur either as a heterogeneous reaction between solid sulphur and oxygen or as a homogeneous process between sulphur vapor and oxygen. For the latter, it is evident that

$$K_P = \frac{P_{SO_2}}{P_S \times P_{O_2}}.$$

In the heterogeneous system with solid sulphur continuously present it is apparent that the partial pressure of the sulphur will remain constant throughout the reaction process and be equal to π_S, the saturated vapor pressure of sulphur at the given temperature. The equilibrium constant of the heterogeneous reaction will therefore be

$$K_P = \frac{P_{SO_2}}{P_{O_2} \times \pi_S}$$

or since π_S is constant at constant temperature,

$$\frac{P_{SO_2}}{P_{O_2}} = K_P \times \pi_S = K_P'.$$

[1] *J. Am. Chem. Soc.*, **46**, 64 (1924).

It is therefore evident that the equilibrium condition for heterogeneous reactions, K_P', can be deduced by inserting the partial pressures (or concentrations, activities, etc.) of the reactants, present only in the gaseous phase, in the mass action relationship. The solid phases present influence the numerical value of the equilibrium constant.

The variation of this constant with temperature can similarly be associated with the variation of the equilibrium constant of the homogeneous reaction with temperature. In the example cited

$$K_P \text{ (homogeneous)} = \frac{K_P' \text{ (heterogeneous)}}{\pi_S}$$

or

$$K_P \cdot \pi_S = K_P'.$$

Now, from the discussion in the preceding chapter,

$$\frac{dlnK}{dT} = -\frac{Q}{RT^2},$$

and, from the Clapeyron-Clausius equation,

$$\frac{dln\pi_S}{dT} = \frac{\lambda_S}{RT^2},$$

where λ_S is the latent heat of vaporization of solid sulphur. Hence,

$$\frac{dlnK_P \cdot \pi_S}{dT} = \frac{dlnK_P'}{dT} = -\frac{Q_P - \lambda_S}{RT^2} = -\frac{Q_P'}{RT^2}.$$

The quantity, Q_P', is the calorimetrically determined heat of reaction between solid sulphur and oxygen to form sulphur dioxide. The variation of K_P' with temperature is similar to that obtaining in the homogeneous system. For short intervals of temperature over which Q' may be regarded as constant the integrated form may be employed.

$$ln\frac{K_1'}{K_2'} = \frac{Q'}{R}\left(\frac{T_2 - T_1}{T_1T_2}\right).$$

If we express Q_P, as in the preceding chapter, in terms of temperature by means of the equation

$$Q_P = Q_0 - qT - \tfrac{1}{2}rT^2 - \tfrac{1}{3}sT^3,$$

it follows that (see page 310)

$$lnK_P = \frac{Q_0}{RT} + \frac{q}{R}lnT + \frac{1}{2}\frac{r}{R}T + \frac{1}{6}\frac{s}{R}T^2 + \cdots + C.$$

In a similar manner, the vapor pressure may be expressed by an equation

$$ln\pi_S = -\frac{\lambda_{0(S)}}{RT} + \frac{k}{R}lnT + \frac{1}{2}\frac{m}{R}T + \frac{1}{6}\frac{n}{R}T^2 + \cdots + C_S,$$

whence it follows that

$$lnK_P' = \frac{Q_0 - \lambda_0}{RT} + \frac{q+k}{R} lnT + \frac{1}{2}\frac{r+m}{R} T + \frac{1}{6}\frac{n+s}{R} T^2 + \cdots + C',$$

where

$$C' = C + C_S.$$

Reference to the preceding chapter will indicate the nature of the magnitudes, q, r, s, $\cdots$. They are the algebraic summations of the m, n, o terms in the equations for the specific heats of the respective substances. For example, when

$$C_P = m + nT + oT^2 + \cdots,$$

we have, in the homogeneous reaction under consideration,

$$-\frac{dQ_P}{dT} = \Delta C_P = (m_{SO_2} - m_S - m_{O_2}) + (n_{SO_2} - n_S - n_{O_2})T + (o_{SO_2} - o_S - o_{O_2})T^2 + \cdots,$$

whence

$$\sum m = q; \qquad \sum n = r; \qquad \sum o = s.$$

In the expression for $ln\ \pi_S$ given above the quantity

$$ln\pi_S = -\frac{\lambda_0}{RT} + \frac{m_S - m_S'}{R} lnT + \frac{1}{2}\frac{n_S - n_S'}{R} T + \cdots + C_S,$$

where m_S, n_S, etc., refer to the respective terms in the expression for the heat capacity of the gaseous form, m_S', n_S', etc., refer to the corresponding quantities in the heat capacity of the solid substance. Hence, it follows that

$$lnK_P' = \frac{Q_0 - \lambda_0}{RT} + \frac{m_{SO_2} - m_{O_2} + m_S'}{R} lnT + \frac{1}{2}\frac{n_{SO_2} - n_{O_2} + n_S'}{R} T + \cdots + C'.$$

For a condensed system, solid or liquid, m' is the heat capacity at the absolute zero, and is, therefore, equal to zero, as specific heat measurements at low temperatures have shown. The equation therefore becomes

$$lnK_P' = \frac{Q_0'}{RT} + \frac{m_{SO_2} - m_{O_2}}{R} lnT + \frac{1}{2}\frac{n_{SO_2} - n_{O_2} + n_S'}{R} T + \cdots + C',$$

where Q_0' is the heat of the heterogeneous reaction at 0° K. In seeking a general solution for such equations and for the corresponding equations for homogeneous equilibria, Nernst suggested that the heat capacity of gaseous systems might be expressed by an equation of the form

$$C_P = a + 2\beta T + R = 3.5 + 2\beta T$$

with a corresponding equation for condensed systems of the form

$$[C_P] = 2\beta' T.$$

This latter is certainly incorrect at low temperatures. In many cases, however, the resulting equation for lnK_P' has been of great utility.

$$lnK_P' = \frac{Q_0}{RT} + \sum \nu 1.75 lnT + \frac{\sum \beta}{R} T + \cdots + \sum \nu I.$$

In its more usual form, as an approximation, this gives

$$\log K_P' = \frac{Q_P'}{4.58T} + \sum \nu 1.75 \log T + \sum \nu C,$$

where the $\sum \nu$ refers to the algebraic summation of the components, resultants positive, reactants negative, existing in the gaseous state alone, C to the integration constants of the vapor pressure equation, employing common logarithms, for the substances existing only as gases in the reaction process, the so-called Conventional Chemical Constants of Nernst.

The Nernst school has normally employed the approximation equation for homogeneous equilibria in the form

$$\log K_P = -\frac{Q_P}{4.571T} + \sum \nu 1.75 \log T + \sum \nu C,$$

and, for heterogeneous equilibria,

$$\log K_P' = -\frac{Q_P'}{4.571T} + \sum \nu 1.75 \log T + \sum \nu C.$$

In these cases K_P and K_P' are defined as $\frac{P_{(\text{reactants})}}{P_{(\text{resultants})}}$, $\sum \nu$ is defined as the algebraic summation of the molecular coefficients of the *gaseous* constituents, reactants positive, resultants negative; $\sum \nu C$ is defined as the algebraic sum of the chemical constants of the *gaseous* constituents, multiplied by the respective molecular coefficients, reactants positive, resultants negative. Thus, in the reaction,

$$CaO + CO_2 = CaCO_3 + Q_P',$$

$$\log K_P' = \log P_{CO_2} = -\frac{Q_P'}{4.57T} + 1.75 \log T + C_{CO_2}.$$

The following are some of the principal values employed by Nernst and his students for the conventional chemical constants.

H_2.....1.6	HCl.....3.0	N_2O.....3.3	CH_4.....2.8
N_2.....2.6	HBr.....3.2	NH_3.....3.3	C_2H_6.....2.6
O_2.....2.8	HI.....3.4	H_2O.....3.6	C_2H_4.....2.8
Cl_2.....3.1	CO.....3.5	H_2S.....3.0	C_2H_2.....3.2
Br_2.....3.2	CO_2.....3.2	CS_2.....3.1	C_6H_6.....3.0
I_2.....3.9	NO.....3.5	SO_2.....3.3	CCl_4.....3.4

The Dissociation of Silver Oxide: This dissociation has been measured by Lewis [1] in the lower range of pressures and by Keyes and Hara [2] over a much wider range. The data have been used by Pollitzer [3] to illustrate the use of the Nernst equation with numerical data shown in the following equation:

$$\log P_{O_2} = -\frac{13{,}130}{4.57T} + 1.75 \log T - \frac{0.010T}{4.57} + 2.8.$$

The agreement with the data of Lewis is shown in the following table.

TABLE XXXIX

P_{O_2} (atm.)	$T_{obs.}$	$T_{calc.}$
20.5	575	567
32.0	598	594
203.0	718	733

Lewis and Randall [4] express the experimental data by means of the equation

$$\frac{\Delta F}{T} = -RlnK = -\frac{7240}{T} - 1.0lnT + 21.95.$$

Gas-Liquid Reactions: The considerations given in the preceding section apply equally well to systems in which the condensed phase is a liquid. Here, also, the expression for K_P' contains the partial pressures of those constituents which appear in the gaseous phase only. Thus, in the reaction

$$2H_2O(g) + S(l) = 2H_2S(g) + SO_2(g),$$

the equilibrium constant

$$K_P' = \frac{P_{H_2S}^2 \times P_{SO_2}}{P_{H_2O}^2}.$$

This reaction has been investigated by Randall [5] at the boiling point of sulphur. The mean value for K_P' at $T = 718°$ K. with the partial pressures expressed in atmospheres was 1.54×10^{-3}. The corresponding magnitude

$$\Delta F_{718} = -RTlnK_P' = 9240 \text{ cals.}$$

Equilibrium between a Solid and an Ideal Solution: The problem of equilibrium between solids and solutions is too complex to be treated adequately at this stage. A comprehensive discussion of ionization and of thermodynamic concentration in solution must precede such an undertaking. This is deferred to subsequent chapters. It is possible, however, to consider the equilibria existing between a solid and an ideal solution of this solid in a suitable solvent.

[1] *J. Am. Chem. Soc.*, **28**, 139, 158 (1906).
[2] *J. Am. Chem. Soc.*, **44**, 479 (1922).
[3] Die Berechnung Chemischen Affinitäten, Ahrens Sammlung, **17**, 414 (1912).
[4] Thermodynamics, p. 481. McGraw-Hill (1923).
[5] Diss. (1912); Lewis and Randall, *J. Am. Chem. Soc.*, **40**, 362 (1918); Thermodynamics, p. 545. McGraw-Hill (1923).

Such an equilibrium is of course an equilibrium between a solid phase and its saturated solution. The change of equilibrium with temperature and pressure is actually the change of solubility with these two variables. It may also be regarded as the freezing point equilibrium of a binary system whose constituents form an ideal solution.

The general equation for the variation of such an equilibrium with temperature is

$$\frac{dlnX_B}{dT} = \frac{L_B}{RT^2},$$

where X_B represents the mol. fraction of the substance B in the binary system AB, L_B is the latent heat of fusion of B at the given temperature, the substance B being that constituent whose pure crystals are in equilibrium with the solution. In ideal solutions there is no heat of mixing of liquids. For a small temperature range over which L_B may be regarded as constant this equation may be employed in the form

$$ln\frac{X_B'}{X_B} = \frac{L_B}{R}\left(\frac{T' - T}{TT'}\right).$$

The equation in this form has been employed by Schröder [1] with good agreement between calculation and experiment. The temperature of the melting point of the pure constituent B is chosen as the temperature T' since under these conditions X_B' is equal to unity. Agreement between calculated and experimental values for L_B becomes, in such cases, a criterion of ideality. Since,

$$\frac{dL}{dT} = \Delta C_P,$$

where ΔC_P is the difference of the molal heat capacities of the substance in the liquid and crystalline states it follows that

$$L_{B(\Delta T)} = L_{B(0)} + \Delta C_P \cdot \Delta T,$$

where $L_{B(0)}$ is the molal heat of fusion at the freezing point of the pure substance B. Under such circumstances,

$$\frac{dlnX_B}{dT} = \frac{L_{B(0)} + \Delta C_P \cdot \Delta T}{RT^2}.$$

This is the general equation for the freezing point lowering of an ideal solution.

This method has also been used by Washburn and Read [2] in the systems benzene-naphthalene, benzene-diphenyl and naphthalene-diphenyl to calculate eutectic temperatures. Excellent agreement between such calculations and experimental observations shows that these systems approach closely to

[1] *Z. physik. Chem.*, **11**, 449 (1893).
[2] *Proc. Nat. Acad. Sci.*, **1**, 191 (1915).

ideality. Johnston and his co-workers [1] have recently shown that the number of such ideal solutions is probably considerably greater than has been hitherto realized. They have shown, for example, that *o*-, *m*- and *p*-nitro-anilines form, in pairs, ideal binary mixtures. Not only may the binary eutectics be calculated, but the ternary eutectic may be calculated thermodynamically. Exact agreement between calculated and experimental solubilities is obtained and between calculated and experimental values for the heats of fusion of the respective compounds.

[1] Dissertations, Yale University, 1923, 1924.

CHAPTER X

THE MEASUREMENT OF ELECTRICAL ENERGY

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All measurements of electrical energy are based on a fundamental law discovered by Ohm in 1827. Ohm's law states that the current in any circuit depends upon two variables, the voltage and the resistance of the circuit. The current has been found to be directly proportional to the voltage and inversely proportional to the resistance. It may be expressed algebraically thus:

$$C = E/R.$$

Exhaustive experiments have shown that Ohm's law holds rigidly for all classes of conductors, so that for the measurement of electrical quantities it is only necessary to define the units and set up the standards. From the algebraic statement of the law it may be seen that the possession of any two of the three units defines the third. The units are based on the c.g.s. system and the electromagnetic relations of the current.

The unit of resistance, the ohm, is based on the c.g.s. system and the electromagnetic units, and was defined by the Electrical Congress at Paris in 1881 as the resistance of a column of mercury one mm. in cross section and weighing 14.4 gms. at the melting point of ice. Under such conditions the length of the column is about 106.3 cm.

The resistance of a metal is very decidedly affected by slight traces of impurities and, as mercury may be more rigidly purified than other metals, it was chosen as the standard. Like all metals, it has a considerable temperature coefficient so that it has been necessary to control definitely the temperature at which the resistance is determined.

Certain alloys have been discovered which have practically no temperature coefficient for ordinary ranges of temperature (manganin and constantin). From these alloys practical resistances have been made and carefully standardized, or compared with the mercury ohm in national bureaus of standards in France, Germany, England and the United States. We have, therefore, most satisfactory and reliable working standards of resistance. Neither the units of current, the ampere, nor of electromotive force, the volt, can be handled in this way. Each one of these units has given rise to a great deal of experimentation and discussion as to accuracy and reproducibility.

Both the ampere and the volt are based upon another law as fundamental as Ohm's law, discovered by Faraday in 1833, which shows the relation between

the current and the amount of chemical reaction that takes place when a current passes from a first class, or purely metallic conductor, to a second class, or electrolytic conductor.

Faraday's Laws of Electrolysis: As a result of the electromagnetic properties of the current, permitting adjustment by observation of the deflection of a galvanometer, it is possible to establish a constant and uniform current, which delivers exactly equal quantities of electricity in equal intervals of time. When such a current is passed through a suitable cell, it has been found to liberate exactly equal amounts of hydrogen in equal time intervals. This same relation holds for metals deposited from solutions or fused salts. From these facts the first part of Faraday's law may be deduced, namely, that the amount of chemical action caused by the current is exactly proportional to the amount of electricity that passes in the circuit. Faraday called this instrument a " volta-electrometer" or voltameter.

The relation just outlined is not the only one discovered by Faraday; for, working with his volta-electrometer in series with cells in which metals were deposited, he found that different amounts of the several metals were deposited for the same amount of electricity. For example: 57.9 gm. of tin were deposited for one gram of hydrogen liberated in the voltameter. This is the equivalent weight of tin, and the weights of the other metals deposited for one gram of hydrogen (the equivalent weight of hydrogen) were found to be the equivalent weights of the metals concerned. These facts led to the second part of Faraday's law—that one and the same current liberates equivalent amounts of the elements, or produces equivalent chemical changes at the electrodes.

Faraday fixed his attention on the decomposition of water, taking the volume of the gases evolved as a measure of the amount of electricity that passed through his voltameter. Experience has shown, however, that there are more suitable reactions for the purpose in view. For example, the weight of a metal deposited from a solution may be more precisely determined than the volume of gases liberated by a current. Silver deposited from a suitable solution, on account of its large equivalent weight, 107.88 grams, and its excellent physical qualities, has proved to be particularly adapted to the measurement of quantities of electricity.

The Silver Coulometer: An exceptional amount of research has been devoted to the silver voltameter, or coulombmeter.[1] The silver is usually deposited in a platinum bowl or cup from a silver nitrate solution, and the increase in weight of the dish due to the deposit of silver is determined. If the current used in depositing the silver is uniform and the time it flowed is noted, then the strength of the current is readily obtained from the relation of coulombs to the weight of silver deposited. In this way the coulometer becomes an ammeter. Due to the exceptional precision of electrical measurements, the coulometer has been subjected to searching investigations as to its reliability.

[1] Coulombmeter is the instrument for measuring coulombs, and this name, proposed by Richards, seems more suitable than the historic term voltameter. The word is generally contracted to coulometer.

Faraday found that there were many secondary reactions at the electrodes which caused apparent exceptions to the exactness of his law, but exhaustive research which has been carried out since 1833 has proved it to be one of the most if not the most exact of our laws.

A very drastic test of the law as applied to different conducting media was performed by Richards,[1] in which silver was deposited from a fused salt at 260 degrees and by the same current from a salt solution at 20 degrees. Four experiments showed an agreement in the deposits of one part in 22,500, or well within the limits of errors of the experiment.

Helmholtz regarded polarization as a most sensitive test of electrolysis. The products of electrolysis tend to recombine and form a counter current which may be detected and measured. Helmholtz found that he could detect in that way the decomposition of as little as 1×10^{-11} gms. of water. From experiments along this line we are justified in concluding that no electricity can pass from a first to a second class conductor without a rigidly equivalent chemical reaction occurring.

Generally, a 15 percent solution of silver nitrate has been used in the bowl for coulometer work and in this solution a piece of pure silver serves as an anode. Pure silver does not dissolve quite completely electrolytically—so that a number of small particles of silver detach themselves from the anode, and thus a certain amount of exceedingly finely divided silver, or slime, is left. In order to keep this slime from the deposit in the bowl, Rayleigh recommended enclosing the anode in filter paper. This brought the solution in contact with cellulose and the question arose of the possible effect of filter paper on the weight of the deposit obtained. This has received a great deal of attention.

The general result has been to direct attention to the purity of the electrolyte as a means of securing reproducible results. Richards and his co-workers, in particular, have advocated surrounding the anode with a cup of porous porcelain to retain the anode slime and to keep the anode liquid away from the cathode. They claim that the anode liquid caused an abnormal result. These effects have not been definitely settled. All these questions have been exhaustively investigated by Smith, Mather and Lowry.[2]

Another question which has received a great deal of attention is the amount and nature of the inclusions in the electrolytic silver. Evidently it has been shown that the deposit is not pure silver but contains small amounts of included water and silver nitrate. The amount would seem to be less than 0.01 percent. This question has been particularly considered by Vinal and Bovard,[3] who also point out that the most accurate value for the absolute electrochemical equivalent of silver is that recommended as the international standard, 1.11800 mg., making the value of the Faraday

$$F = 96{,}494.$$

[1] *Proc. Am. Acad. Arts Sci.*, **38**, 413 (1902).
[2] *Proc. Roy. Soc.*, **207**, 546 (1908).
[3] *J. Am. Chem. Soc.*, **38**, 496 (1916).

If the amount of the impurity were constant, it would not matter from the standpoint of measuring the quantity of electricity. Evidently, from the exhaustive work of Smith, Mather and Lowry (*loc. cit.*) it is possible to prepare solutions of silver nitrate which yield deposits of silver reproducible in mass to 1 or 2 parts per 100,000.

The conclusions concerning the best method of conducting the determination of current by means of the silver coulometer are given by Rosa and Vinal.[1] The porous cup and the F. E. Smith forms of voltameter are the most satisfactory. Electrolyte of the highest possible purity is essential. If it is pure, the weight of deposit is independent of the size of the voltameter; if impure, it is larger with large voltameters (volume effect). The temperature coefficient is zero. If the electrolyte is pure, the inclusions within the deposit average 0.004 per cent of its weight. The proposed specifications are in part:

> The electrolyte shall contain 10 to 20 grams silver nitrate in 100 cc. of solution and shall be free from organic or other reducing substances and colloids as shown (1) by testing with 1 cc. of 0.001 *N*. $KMnO_4$ added to 10 cc. of 66 per cent silver nitrate solution acidified, (2) by yielding an unstriated deposit, (3) by absence of the volume effect. Silver nitrate is purified by crystallization from acid solution and fusion, repeatedly, if necessary. The voltameter should contain not less than 75 cc. in the cathode chamber and the concentration at the surface of the cathode should not be reduced during electrolysis below 5 per cent. The electrolyte should be neutral or but slightly acid (1 part in 1,000,000) as tested by methyl red (0.2 per cent in alcohol) or iodeosin (10 mg. per liter) in ether, after removal of the silver by neutral potassium chloride. The electrolyte must be neutral or slightly acid at the end of the experiment. The anode should be of pure silver and is preferably coated with electrolytic silver. It should have as large an active area as the instrument permits. The current should be constant and not more than 1 ampere for not less than 1 hour. After washing, the cathode bowls should be dried at 150° C.

The only other coulometer which has received careful study is the iodine coulometer.

The Iodine Coulometer: Washburn and Bates[2] have shown that an iodine coulometer is capable of a reproducibility of 0.002 per cent for the iodine liberated at the anode in a potassium iodide solution. In addition, the iodine surrounding the cathode in the potassium iodide solution disappears. The change in the amount of iodine at either electrode may be accurately measured by titration. It was shown that the change in the amount of iodine at the anode and the cathode checked to within three parts in a hundred thousand. This constitutes a unique check on the accuracy of the determination and the correctness of the assumed electrochemical reactions. The iodine coulometer as used by Washburn and Bates was directly compared with the silver coulometer used at the Bureau of Standards at Washington where so much exhaustive work has been done on the silver coulometer.[3] The silver deposited in the coulometer was directly compared with the iodine liberated by the same current and measured by titration, thus giving a direct comparison of the equivalent weights of iodine and silver, which, for these elements, should be

[1] *Bull. Bur. Standards*, **13**, 479 (1916); *Sci. Paper 285*.
[2] *J. Am. Chem. Soc.*, **34**, 1341 (1912).
[3] *J. Am. Chem. Soc.*, **36**, 916 (1914); *Bur. of Standards, Sci. Paper 218*.

the same as their atomic weights. The coulometer comparison gave the ratio of silver to iodine as 0.85017 while the best figure for the atomic weights by chemical methods appears to be 0.84998. The difference is well within experimental errors and constitutes a most satisfactory agreement between chemical and electrochemical values.

The Absolute Measurement of Current: All of this gives only a precise and reproducible method of measuring a current and must be compared with the value of the current in absolute or c.g.s. units. From the electromagnetic action of the current the following convention has been agreed upon: In a conductor one cm. of which is in the form of an arc of one cm. radius, the current which produces a force of one dyne on a unit magnetic pole at the center of this arc is defined as the electromagnetic unit of current. For practical purposes this is too large a unit, so the ampere commonly used is one tenth of the electromagnetic unit.

A conductor carrying a current behaves as a magnet. If two coils in the form of helices are arranged co-axially, a current passing through them in series causes them to act on each other with a force which may be calculated in absolute or c.g.s. units, from a knowledge of the dimensions of the coils and the current employed. Or, if we know the force and the dimensions of the coils, the current may be calculated. If one coil is fixed and the other suspended from the beam of a balance, the force due to a given current may be measured in gravitational units. Such a current weigher has been constructed by Ayrton, Mather and Smith.[1] The following extracts from their paper will indicate the historical development and the use of this instrument.

A current can be measured absolutely in the electromagnetic system of units either by means of the action of the current on a magnet or of the current on a current. The former method has the disadvantage that at least two independent measurements are necessary. For example, in using an electromagnetic balance, the strength of the magnet acted on by the electric circuit has to be determined, as well as the force exerted on the magnet by the circuit. In galvanometers, either of the sine or tangent type, the magnetic field produced by the electric circuit is compared with the earth's horizontal field, the strength of which is determined independently. Further, as the strength of artificial magnets cannot be regarded as truly constant, and the earth's field is subject to diurnal and secular variations, this class of measurement is not ideal.

In the electrodynamic class of measurement the mutual action between two or more coils carrying current takes the form of a torque, as in electrodynamometers, or a direct force, as in current weighers. In electrodynamometers, the torque may be measured with a bifilar suspension, the torsion of a wire or spring, or by means of a gravity balance. Current weigher measurements are almost always made by direct comparison with gravity, which is believed to be constant, and is known to a higher degree of accuracy than the strengths of any magnet or magnetic field that has yet been measured.

[1] *Proc. Roy. Soc.*, **207**, 464 (1908).

Shortly after the absolute system of units was devised by Gauss and Weber in 1832, A. Becquerel weighed the attraction between a coil and a magnet; and two years later Lenz and Jacob used and modified Becquerel's balance by arranging a coil and magnet at each end of the beam. In 1840 W. Weber determined the electrochemical equivalent of water, using the tangent galvanometer as his instrument for measuring current; and in 1843 similar measurements were made by Bunsen and by Casselmann, followed in 1851 by Joule.

Meanwhile W. Weber had, in 1846, invented his two forms of electrodynamometer, one with the suspended coil inside, and the other with this coil outside the fixed coil, and he measured the torque with bifilar and unifilar suspensions.

The first current weigher appears to have been constructed by Cazin in 1863. In 1864 Joule made a current weigher having three circular flat coils wound with copper strip, one being suspended from a balance, so that its mean plane, which was horizontal, was midway between those of the other two fixed coils. This instrument had the correction to its principal constant determined by comparison with a standard tangent galvanometer, and was employed in Joule's electrical determination of the mechanical equivalent of heat. Its object was to enable a constant current to be maintained through the calorimeter, independent of variations in the earth's magnetic field.

The subject attracted considerable attention from this time onward, as is evident from the researches of Latimer Clark,[1] Kohlrausch,[2] Mascart,[3] Lord Rayleigh [4] and Mrs. Sidgwick,[5] Gray,[6] Pallet and Potiers,[7] Heydweiller,[8] Kahle,[9] Jones and Ayrton.[10] More recent determinations are due to Paterson and Guthe[11] employing a torsion electrodynamometer and to Guthe[12] (1906) using a modified Gray electrodynamometer.

The current balance of Ayrton, Mather and Smith may now be described.

The instrument consists of a very sensitive physical balance supporting a coil with vertical axis from each end of the beam, these coils hanging coaxially within fixed coils carried from the base of the balance. A diagrammatic sketch of the arrangement is shown in Fig. 1.

From the diagram it will be seen that the current flows in opposite directions in the upper and lower parts of the outer coils. On the left-hand side of Fig. 1 the current in the upper half of the outer coils flows clockwise (looking from above) and in the lower half counter-clockwise, whilst in the left-hand suspended

[1] *Proc. Roy. Soc.*, May 30, 1872; *Phil. Trans.*, 1874, Part I.
[2] *Pogg. Ann.*, **170** (1873).
[3] *Jour. de Phys.*, (2) **1**, 109 (1882).
[4] *B. A. Report*, p. 445 (1882).
[5] *Phil. Trans.*, 175, 411 (1884).
[6] *Phil. Mag.*, **22**, 339 (1886).
[7] *Jour. de Phys.*, VI, 175, and IX, 381 (1890).
[8] *Wied. Ann.*, **44**, 533 (1891).
[9] *Wied. Ann.*, **59**, 532 (1896).
[10] *B. A. Report*, Bristol, 157 (1898); *Jour. Inst. Elec. Eng.*, **35**, 12 (1905).
[11] *Phys. Rev.*, **7**, 257, 1898.
[12] *Phys. Rev.*, **9**, 288, 1899.

coil the circulation is shown clockwise. The tendency is, therefore, to lift the suspended coil *SL*. It will also be seen that the outer coils on the right will tend to depress the suspended coil *SR*, so that the two sets of coils exert a clockwise torque on the beam. This torque is balanced by weights added to or taken from scale pans supported independently on the knife edges which carry the suspended coils, an arrangement which avoids displacement of the suspended coils when the weights are placed or removed.

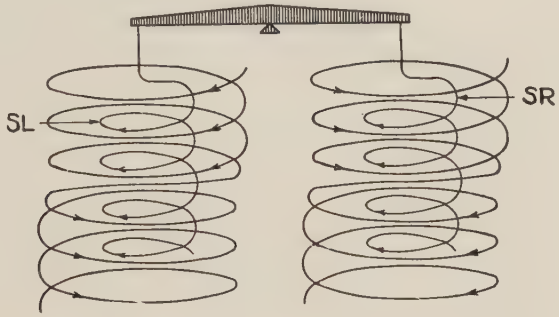

FIG. 1. Diagrammatic Illustration of Current Balance

All the coils are wound with bare wire on hollow marble cylinders, having double-threaded screw grooves cut on the surfaces, into which separate wires are laid as shown in Fig. 2. In this figure one wire is indicated by two thin lines, and the other is shown thick. The two wires, hereafter distinguished as No. 1 and No. 2, form two adjacent helices which, in the use of the instrument, are connected in series and act as one coil. They can, however, be readily disconnected from each other and an insulation test made between them. This applies to each of the six coils forming the current weigher, arrangements being made whereby the six No. 1 wires may be connected together, the six No. 2 wires similarly grouped, and the insulation between adjacent wires of the whole instrument tested simultaneously. Any leakage between the two adjacent helices can thus be readily detected and localized and remedied.

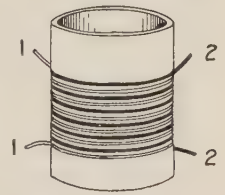

FIG. 2. Method of Winding Coils

Each of the fixed cylinders carries four helices, two upper and two lower, and each suspended cylinder two. There are therefore twelve helices in all, and these are connected in series, in the normal use of the current weigher, by means of small concentric cables running to a plug board and commutators outside the balance case. Flexible connections are used as leads and returns to and from the suspended coils. The commutators enable the direction of the current in any coil to be changed at will. By reversing the current in the coils on the fixed cylinders the forces between the fixed and suspended coils are reversed, and the apparent change of weight thus produced is a measure of the square of the current used.

The same current weigher was used by Smith, Mather and Lowry in their exhaustive investigation of the silver voltameter. They were thus able to measure their current in absolute units and concluded that their measurements and results were reliable to 2 parts in 100,000. They found that the ampere current deposited .00111827 gram of silver in one second. This is the amount of silver deposited by a coulomb—an ampere per second. Now, if we divide the equivalent weight of silver by their figure, $\frac{107.88}{.00111827} = 96{,}471$ coulombs per gram equivalent, which would be the same for the equivalent of any element or for any chemical reaction. This quantity is a fundamental constant of electrochemical action and is known as the Faraday.

Guthe (*loc. cit.*) summarizes the theory of the use of the electrodynamometer in these words: "As was first pointed out by Gray the expression for the torque between the two coils of an electrodynamometer assumes a simple form if the dimensions of both coils are chosen so that the length and the radius are in the proportion 3 : 1, if their centers coincide and, finally, if the dimensions of the fixed coil are large in comparison with those of the movable coil. Under these conditions the expression for the torque between the two coils with their axes at right angles to each other becomes

$$T = \frac{4\pi^2 N n r^2}{D^2 + L^2} I^2,$$

where N and n are the number of turns in the stationary and movable coils, D and L the diameter and length of the stationary, r the radius of the movable coil, and I the current, expressed in c.g.s. units."

Previously many determinations of the current have been made in absolute units and expressed in weight of silver per coulomb.

		Milligrams
Mascart	1884	1.1156
Kohlrausch	"	1.1183
Rayleigh and Sidgwick	"	1.1179
Pallet and Potiers	1890	1.1192
Kahle	1899	1.1183
Paterson and Guthe	1898	1.1192
Pallet and Deduc	1903	1.1182
Guthe	1906	1.1182

These determinations were made by the use of the tangent galvanometer and the electrodynamometer. It appears therefore that our knowledge of the current in absolute units is satisfactorily known.

The Measurement of Electromotive Force: Congresses have defined the ampere as that unvarying current which deposits 0.001118 gram of silver per second in a coulometer of definite specifications. A perusal of the work done on the coulomb indicates that, for high precision, one must use exceptional facilities and great experimental ability. Attempts have therefore been made to develop units of electromotive force and with somewhat more favorable

results from the standpoint of practical measurements, since standard cells may be constructed which are satisfactorily reproducible. A voltaic cell is a combination of metallic conductors or electrodes joined by an electrolyte and the possible reactions at the junctions of the electrolyte and metallic conductors furnish the electromotive force and the current. From the standpoint of thermodynamics a definite chemical reaction should give a definite electromotive force to the cell. It is, however, not only the purely chemical reactions which take place at the electrodes, but all other changes occurring that take part in the generation of current. For example: it would seem that two perfectly pure pieces of silver in a uniform silver nitrate solution should give zero potential and no current when joined externally, but this is not so, though the chemical reactions at the electrodes must be the same. It is generally found that two pieces of silver from the same pure silver wire show an electromotive force when opposed in any silver solution. Presumably, there are certain strains or physical differences which account for this, since annealing the electrodes causes the electromotive force to diminish markedly. Soft metals show better agreement than hard metals. Pure mercury electrodes show the best agreement, and amalgams are more satisfactory than metals in this respect. In general a liquid electrode is necessary where precision and reproducibility are required. The old Daniell cell, amalgamated zinc in zinc sulphate, copper sulphate, copper,

$$\mathrm{Zn.Hg}\,|\,\mathrm{ZnSO_4\ aq.}\,|\,\mathrm{CuSO_4\ aq.}\,|\,\mathrm{Cu},$$

was long a working standard, but it did not have the constancy or reproducibility demanded by the precision possible in electrical measurements. A much more reproducible and constant cell was proposed by Latimer Clark in 1872. The Clark cell was composed of a negative pole consisting of an amalgamated zinc electrode in a saturated zinc sulphate solution, and, for the positive pole, mercury covered with mercurous sulphate in zinc sulphate solution. The mercury constitutes a liquid electrode, and the zinc amalgam is also essentially a liquid electrode. Thus, many sources of irregularity were eliminated. This cell gave a voltage of 1.433 volts at 15 degrees, but diminished by about 0.001 volt per degree between 15 and 25 degrees. A rigid temperature control was therefore necessary. Edward Weston in 1892 found that, by replacing zinc by cadmium throughout, a cell was obtained with a temperature coefficient only about one thirtieth of that of the Clark cell. In fact, by replacing the crystals of cadmium sulphate and the saturated solution by an unsaturated solution of cadmium sulphate of a definite strength, an unsaturated cell of practically no temperature coefficient for ordinary temperatures was obtained. While this cell has not the reproducibility of the saturated cell, it is reasonably constant and may be calibrated and thus compared with manganin resistances as a working standard.

Like the coulometer, the standard cell has received a great deal of attention. The investigations have shown that the materials used in the cell and their assembling need very precise specifications. In the Clark cell the negative

electrode seems to be perfectly reproducible and constant. Zinc amalgam, amalgamated zinc and pure zinc all seem to have the same potential in the zinc sulphate solution.[1] A 10 per cent amalgam has generally been employed with a fused-in platinum wire as contact. Fig. 3 shows the usual form (or H

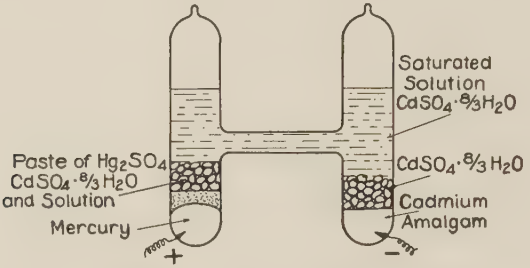

FIG. 3. Diagram of Weston Saturated Cadmium Cell

cell) provided with suitable lead wires soldered to the fused-in platinum wires. This cell may be immersed in an oil bath where the temperature remains constant and can be rigidly controlled.

Freshly prepared cells were observed to have a higher electromotive force than seasoned cells from the same materials. The trouble was found to be in the cathode or mercury leg of the cell. Zinc sulphate is a very stable and reproducible salt, but this is not so with the mercurous sulphate used to cover the mercury as a depolarizer, for this salt readily hydrolyzes. In assembling the cell it was customary to wash mercurous sulphate with water, mix with zinc sulphate crystals and a saturated solution of zinc sulphate to form a paste. This procedure inevitably left some basic salt in the depolarizer and it was this salt which was responsible for giving the cell its initial high value. The first attempt to exclude the basic salt in preparing the mercurous sulphate and to exclude it in assembling the cell was made by Carhart and Hulett.[2] These precautions permitted the construction of cells which showed their normal electromotive force immediately a definite temperature was obtained. The cells also agreed among themselves to 1 part in 100,000. Equally satisfactory results were obtained with the cadmium or Weston cell.

The reproducibility of the standard cell invites a detailed consideration of the mechanism of the changes that take place in them when the current passes. In the Clark cell, the negative or zinc electrode is usually 10 per cent zinc amalgam which is a two-phase electrode, made up of zinc and saturated liquid amalgam which contains 2.22 per cent of zinc at 25°. It is this liquid amalgam which controls the potential of the electrode, as amalgams with less zinc give less potential, according to the Nernst logarithmic relation.[3] Evidently the two-phase amalgam adjusts itself to equilibrium very rapidly and

[1] See, however, Cohen and von Grimmeker, *Z. physik. Chem.*, **75**, 437 (1910).

[2] *Trans. Am. Electrochem. Soc.*, 5, 59 (1904).

[3] *J. Phys. Chem.*, **14**, 158 (1910).

exactly on change of temperature; so, this electrode is very reproducible and stable. The potential of the zinc electrode also varies with the concentration of the zinc sulphate in the electrolyte, but here again the solid zinc sulphate, $ZnSO_4.7H_2O$ maintains a saturated solution which also gives a definite, reproducible concentration for each temperature. Nor does it appear that traces of impurities have a measurable effect on this electrical potential. The reaction that takes place on the passage of the current is the formation of $ZnSO_4$, and this is the main energy change in the cell. As will be subsequently discussed, the $ZnSO_4$ formed changes to the hydrate $ZnSO_4.7H_2O$.

In the positive or cathode leg of the cell there is a solution saturated with respect to zinc sulphate and also with respect to mercurous sulphate in contact with the mercury electrode. The concentration of mercury ions in the electrolyte seems to be the controlling factor; so, attention has been directed to the purity of the mercurous sulphate which controls this concentration. The solubility is small, so that a slight variation in the purity or properties of the mercurous sulphate makes a measurable variation in the concentration of the mercury ions in the cathode leg and so in the voltage of the cell. The reaction that takes place at this electrode on the passage of the current is the decomposition of mercurous sulphate. A most precise and satisfactory insight into the workings of this cell has been formulated by means of a thermodynamical study.[1] Since the voltage in absolute units and the temperature coefficient are so accurately known, the Gibbs-Helmholtz relation is most suitably applied:

$$E = -\frac{\Delta H}{nF} + T\frac{dE}{dT},$$

where ΔH = the amount of heat energy absorbed, n = the valence and F = the Faraday.

In calculating the chemical energy by the use of this formula and the observed values of the cell a discrepancy of some 4000 cal. was found on assuming that the reactions were the formation of $ZnSO_4$ at the anode and the decomposition of Hg_2SO_4 at the cathode. However, one must consider that the $ZnSO_4$ formed at the anode was anhydrous and would interact with the solution, combining with the water to form $ZnSO_4.7H_2O$, and that removing water from the saturated solution would cause some of the salt to crystallize out. Both these changes are accompanied by marked thermal changes. When these were determined and taken into account, the agreement between the calculated and observed values was most satisfactory, so that our knowledge of the reaction at the electrodes in this cell is quite complete.

The Weston, or cadmium, cell is very similar to the Clark cell in many respects, but the cadmium amalgam used as the anode is not as simple as the zinc amalgam. It was found by Bijl [2] and Paschen [3] to be a much more complicated system. Cadmium amalgams of between 5 and 15 per cent of cadmium

[1] E. Cohen, *Z. physik. Chem.*, **54**, 62 (1900).
[2] *Z. physik. Chem.*, **41**, 641 (1902).
[3] *Z. anorg. Chem.*, **36**, 201 (1903).

at ordinary temperatures consist of a liquid and a solid phase. The solid phase is not cadmium, but an isomorphous mixture of cadmium and mercury, which, however, has a very definite composition for each temperature and yields a very definite and reproducible liquid amalgam for any ordinary temperature. In fact, the potential of the usual 12 per cent cadmium amalgam against a saturated cadmium sulphate solution is most satisfactorily constant and reproducible. Tests on old cells which have changed in voltage have always shown that the amalgam potentials were entirely normal. The anode potential depends upon the concentration of mercury ions in a saturated cadmium sulphate solution surrounding the mercury anode and this has been found to be a complicated system. The main reactions in the Weston cell are the formation of $CdSO_4$ at the anode and the decomposition of the Hg_2SO_4 at the cathode, and the difference in the heats of these two reactions furnishes the bulk of energy of the cell. Profiting from the experience with the Clark cell, one must consider that the anhydrous cadmium sulphate formed at the anode will remove water from the saturated cadmium sulphate solution and cause a crystallization of some $CdSO_4.8/3H_2O$. Both of these changes are accompanied by measurable thermal changes and contribute to the energy of the cell. These heat reactions were taken into consideration by Cohen [1] but even then the agreement between the sum of all these heat changes and the electrical energy was unsatisfactory. The calculations had been based on the heat of formation of cadmium sulphate from metallic cadmium. But, in the cell, the cadmium sulphate is formed from cadmium amalgam and it was shown that some energy is required to remove cadmium from the amalgam. For, the potential between cadmium and cadmium amalgam opposed to each other in a cadmium sulphate solution is considerable. By using the potential of such a cell and its temperature coefficient it was possible to allow for this energy difference which was over 5000 cal. The agreement between the thermal data and the electrical energy of the cell was then most satisfactory. Here again therefore the thermodynamic treatment has given a clear insight into all the changes that take place in the cell. In the Clark cell, the amalgam has the same potential against a zinc sulphate solution as has pure zinc, so there is no correction needed for this factor in calculating the energy of the Clark cell.

Many other combinations have been considered for standards of electromotive force, but nothing has been found to compare in reproducibility or constancy with zinc or cadmium cells. It has been pointed out that metals in the solid state are not suitable for constant electrodes, so that mercury is preeminently fitted to be one of the electrodes in a standard cell and a liquid amalgam must form the other. In order to secure sufficient voltage, the base metal chosen must be as far removed as possible from mercury in the voltaic series. It should also exist only in one stable state of oxidation. The metals that best satisfy these conditions are zinc and cadmium. The depolarizer which covers the mercury must be a salt of mercury. It should not have too great a solubility, and must be well defined physically and chemically, so as to yield a

[1] *Z. physik. Chem.*, **34**, 612 (1900).

rigidly definite concentration for each temperature. Of the salts of mercury, mercurous sulphate seems most nearly to meet these requirements. If the depolarizer is a sulphate, the salt of the base metal which furnishes the solution must also be a sulphate. It therefore appears that the choices are decidedly limited and it seems improbable that other combinations as suitable as the Clark or the cadmium cell will be found. These two cells have shown a reproducibility of one part in ten thousand and there is some evidence to show that the Clark cell is the more constant of the two. The cadmium cell has shown more tendency to change with time, some cells of every set decreasing to low values and becoming useless as standards. An extended investigation[1] of this phenomenon showed that some chemical change, probably a slow hydrolysis of the mercurous sulphate, takes place in the cadmium sulphate solution. It appears to be a very slow reaction, though probably more rapid at the mercury electrode and surfaces. The essential facts are that if the content of the cathode system of the cell, Hg_2SO_4, hydrated cadmium sulphate, saturated solution and mercury, be thoroughly stirred, the voltage of the cell increases by about two millivolts. If the solids are now allowed to settle on the mercury electrode, the voltage of the cell decreases slowly with time, but does not stop at the value ordinarily obtained for the cadmium cells, but decreases to much lower values. The Clark cell seems to be quite free from these defects. It therefore seems probable that cadmium sulphate slowly hydrolyzes the mercurous sulphate and equilibrium is not obtained in the cathode system of the cell. However, a set of cadmium sulphate cells made with proper precautions should agree to one or two parts in 100,000, and many of these remain constant for years. It is necessary to make new sets at intervals as a check on the old cells. More work is needed to discover the exact nature of the changes which take place. A Clark cell while free from these defects has a much greater temperature coefficient and the cell shows a tendency for the glass to crack where the platinum lead wires are sealed in to make contact with the zinc amalgam. This cracking is presumably due to an alloying of zinc with platinum, resulting in a change of volume. This factor has generally ruined some cells of every set.

International electrical congresses have devoted much attention to the cadmium or Weston standard cell on account of its low temperature coefficient and favorable characteristics. An important international conference was held in Washington at the National Bureau of Standards in 1910 with representatives from England, France and Germany present. Not only were the outstanding faults of the silver coulometer and the standard cells considered, but a considerable amount of experimental work was done on these problems and published in the Report to the International Committee on Electrical Units and Standards, Dept. of Commerce and Labor, Bureau of Standards, January 1, 1912. Specifications for the silver coulometer are considered and the value of the electromotive force of the Weston standard cell, as based on the coulometer, was given as 1.0183 volts at 20°. From investigations pre-

[1] *Phys. Rev.*, **27**, 337 (1908).

viously carried out and work done at the conference, a reproducibility of 1 or 2 parts in 100,000 would seem to be obtainable, although there are still outstanding problems of divergencies with both voltameter and the standard cell.

The value of the electromotive force of standard cells in absolute units has been determined many times. The constant current has been determined by the electrodynamometer or the ampere balance, or has been based on the silver coulometer. When such a current passes over a known resistance there is a conventional fall of potential of 1 volt per ohm, the international volt being so defined and measured. The conventional value of the Weston cell was found to be 1.0183 volts at 20° and the change with temperature of these cells has been carefully determined by Wolf and Waters[1] as follows:

$$E_t = E_{20} - .0000406(t - 20) - .00000095(t - 20)^2 - .00000001(t - 20)^3.$$

For very precise work one must employ a thermostat capable of holding the temperature constant to 0.01°. As standard cells often take a considerable time (days) to attain their proper value at a given temperature, it is found necessary, for most precise work, to construct a number of cells and place them in a thermostat which would keep them constantly within 0.01° of a suitably chosen temperature. This is quite possible with modern thermostats[2] so that it is possible for the different laboratories to establish voltages which agree most satisfactorily. This is shown from the report of the meeting of the International Committee at Washington, 1910.

With this basis, precision measurements may be made of any other electrical quantities. The determination of voltage is accomplished by the zero, or Poggendorff method, where the standard cell is opposed to a fall of potential over known resistances (Fig. 4). The current from the battery, B, is passed over a resistance, AC; a shunt joined at A includes the cell and a sensitive galvanometer, G, and is joined to the resistance with a sliding contact, X, so that the electromotive force of the standard cell opposes the fall of potential over AX. The galvanometer, G, indicates the point at which there is a balance, and, if calibrated resistances are used, one knows the fall of potential over each ohm in the circuit. Supposing the cell is a Weston standard at 20° with an electromotive force of 1.01830 volts and one makes $AX = 10{,}183$ ohms, adjusting the resistance XC until balance is obtained; the potential fall over each ohm is exactly .0001 volt and it is readily seen that, using suitable resistances, such a method is capable of measuring voltages greater as well as less than the standard cell. The accuracy depends upon the accuracy of the resistances and the sensitiveness of the galvanometer. Perhaps no other physical measurements made are as accurate or satisfactory as those made by the compensa-

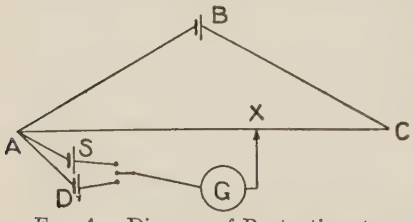

Fig. 4. Diagram of Pontentiometer Measurement

[1] *Bull. Bur. of Standards*, 5, 309 (1908).

[2] *Phys. Rev.*, 32, 276 (1911).

tion potentiometer method. It is a simple matter to measure accurately the voltage of any other cell by putting it in place of a standard cell, once the fall of potential has been determined. The Weston unsaturated cell is calibrated in this way, and then used as a working standard; it is, of course, necessary to maintain a steady and uniform current from the battery, B, through the circuit and this is tested from time to time by means of the standard cell.

CHAPTER XI

CONDUCTANCE, IONIZATION AND IONIC EQUILIBRIA

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Almost immediately after the discovery of the Voltaic pile,[1] Nicholson and Carlisle [2] decomposed water by a current from the pile passing between platinum and gold wires immersed in that liquid. Cruickshank[3] at the same time showed that metallic salts could be decomposed by the pile, and that during the decomposition of water the liquid became alkaline around one wire and acid around the other. This puzzling result was first explained by Humphry Davy,[4] who began experiments with the pile in 1800, and showed that decompositions could be effected in different vessels provided these were connected by strips of moist animal or vegetable substances, asbestos, or even the two hands of the experimenter.[5] In a careful research, carried out in 1806, Davy showed [4] that the acid and alkali were produced from impurities in the water, and that "water, chemically pure, is decomposed by electricity into gaseous matter alone, into oxygen and hydrogen." He found that [6] acids could be passed through alkaline solutions and *vice versâ*, and that apparently insoluble substances, when moist, were decomposed by the electric current. His experiments convinced him of the great decomposing power of the pile, and led to the isolation of the alkali metals. Davy gave no detailed theory of the phenomena observed, and Faraday later on remarked [7] that "probably a dozen precise schemes of electrochemical action might be drawn up, differing essentially from each other, yet all agreeing with the statement there given" [by Davy].

After a period of mystification it became clear that voltaic electricity was fundamentally the same as frictional electricity, as had all along been maintained by Volta, and this was proved by experiments of Wollaston,[8] who showed that the effects produced by each were the same, and in particular that

[1] *Phil. Trans.*, **90**, 403 (1800); Righi, Volta e la pila, Como, 1899.
[2] *Nicholson's J.*, **4**, 179 (1800).
[3] *Ibid.*, **4**, 187 (1800); Henry, *ibid.*, **4**, 223 (1800).
[4] *Phil. Trans.*, **97**, 1 (1807); Works, ed. J. Davy, vol. 5, p. 1.
[5] *Nicholson's J.*, **4**, 294 (1800); Works, **2**, 139; *Phil. Trans.*, **91**, 397 (1801).
[6] *Phil. Trans.*, **97**, 1 (1807); Works, **5**, 1.
[7] *Phil. Trans.*, **123**, 684 (1833); Experimental Researches, Series 5, p. 136.
[8] *Phil. Trans.*, **91**, 427 (1801).

frictional electricity could produce chemical decomposition. Water had previously [1] been decomposed by sparks by van Trostwyk and Diemann, but in this case both gases were evolved from each electrode. In 1802 Erman [2] showed that the voltaic pile could affect a gold leaf electroscope. Any remaining doubts were set aside by an elaborate research by Faraday,[3] who realized clearly that the only difference between the effects produced by frictional and voltaic electricity was due to differences in quantity and intensity (voltage or potential). The frictional machine produced a very small quantity of electricity at high intensity, whilst the pile or battery produced a much larger quantity at a much lower intensity. The distinction between quantity and intensity, so fundamental in the study of electricity, was first made by Cavendish.[4]

Systematic researches on the decomposition of dissolved substances by the electric current were made by Hisinger and Berzelius in 1804.[5] They showed that acid or halogen always appeared at one pole, and alkali, metal, or hydrogen at the other. The products of decomposition appeared only at the poles.

Conductors and Non-Conductors: The distinction between conductors and non-conductors of electricity was first made experimentally by Stephen Grey [6] (1728–1736). The names were first used by Desaguliers in 1739.[7] Good conductors are metals, many sulphides such as galena and pyrites, aqueous solutions of acids, bases and salts, fused salts, and water when not perfectly pure. Bad conductors, or insulators, are dry solid salts, metallic oxides, ice, some metallic compounds, such as $SnCl_4$, $AsCl_3$, HgI_2, As_2S_2, and As_2S_3,[8] most non-metallic elements, pure water, most organic compounds, mica, and glass, all at the ordinary temperature. A large number of substances were examined and classified by Hampe.[9]

A curious relation between conducting power and optical properties was pointed out by Maxwell:[10] transparent substances are usually insulators. Light, according to Maxwell's theory, consists of electromagnetic energy, and if the substance through which it passes is a conductor, the electric displacements in the light wave generate electric currents in the material, which are dissipated as heat and thus the light is extinguished. Metals, which are opaque to light, are good conductors of electricity. In insulators, the electrons

[1] *Gren's J.*, **2**, 130 (1790); cf. Strong, *Amer. Chem. J.*, **50**, 213 (1913).

[2] *Gilb. Ann.*, **11**, 90 (1802).

[3] *Phil. Trans.*, **123**, 23 (1833); Expt. Res., 3d Series, p. 76.

[4] *Phil. Trans.*, **66**, 196 (1776); Collected Papers, ed. Maxwell and Larmor, Cambridge, 1921, vol. 1, p. 200.

[5] *Ann. Chim.*, **51**, 167 (1804).

[6] Priestley, History of Electricity, 2d edit., London, 1769, p. 25.

[7] Priestley, *ibid.*, 62; on early history see J. C. Fischer, Geschichte der Physik, 8 vols., Göttingen, 1801–1808.

[8] Faraday, *Phil. Trans.*, **123**, 507 (1833); Expt. Res., 4th Series, 110 ff., 7th Series, 201.

[9] *Chem. Z.*, **11**, 54 (1887); **12**, 1 (1888); Lorenz, Die Elektrolyse geschmolzener Salze, Halle, 1905–6; 3 parts; part 2, p. 182.

[10] Treatise on Electricity and Magnetism, Oxford, 1892, vol. 2, p. 446; Jeans, Electricity and Magnetism, Cambridge, 1911, 534.

are bound and there are only displacements, not convective motion, of them, whereas in conductors the electrons actually move. Good metallic conductors are also good reflectors of light.[1] An apparent exception to the rule is exhibited by solutions of electrolytes, which are good conductors yet are transparent. In this case, however, the electricity moves in connection with material particles, the ions.

Classes of Conductors: Early experimenters, such as Davy, noticed that conductors could be divided into two classes: (i) those in which the electricity moves without producing chemical changes; (ii) those in which chemical changes always accompany the passage of the current. Metals are typical of the first class, called *metallic conductors.* The second class comprises what are called, following Faraday,[2] *electrolytes*, or *electrolytic conductors.* Davy[3] noticed that the conductivity of metals diminishes with rise of temperature, whilst Ohm[4] found that of electrolytes to increase. Carbon is the principal exception to this rule: it conducts metallically but its conductivity increases rapidly with rise of temperature.[5] Silicon also shows this peculiarity.[6] Tellurium shows first an increase up to 70–80°, then a decrease, in conductivity with further rise in temperature.[7] The case of selenium, the resistance of which varies on exposure to light,[8] is well known. Some sulphides conduct metallically and others electrolytically, both solid and in the state of fusion. The latter increase in conductivity with rise of temperature.[9] Some peculiar results were noticed by Hittorf.[10] The conductivity of copper sulphide is increased by traces of free sulphur and the conductivity of the native sulphide depends on free copper. Silver sulphide appears to conduct metallically because of the formation of fine threads of silver. The supposed metallic conduction of fused silver halides is also due to threads of silver stretching from pole to pole.[11]

Unipolar Conduction: A peculiar class of conductors are those known as *unipolar*, which allow electricity to pass from one electrode only. Erman[12]

[1] N. R. Campbell, Modern Electrical Theory, Cambridge, 1913, 60.

[2] Expt. Res., 4th and 5th Series, p. 110; the nomenclature is introduced in Series 7, p. 197.

[3] *Phil. Trans.*, **111**, 431 (1821).

[4] *Ann. Physik*, **63**, 389 (1844).

[5] Cf. Muraoka, *Ann. Physik*, **13**, 307 (1881); S. P. Thompson, *Lumière électrique*, 22, 621 (1886); Dewar and Fleming, *Phil. Mag.*, **34**, 326 (1892).

[6] Le Roy, *Compt. rend.*, **126**, 244 (1898); *Z. Elektrochem.*, **5**, 95 (1898).

[7] Exner, *Wien. Ber.*, **73**, 285 (1876); Lenher and Morgan, *J. Am. Chem. Soc.*, **22**, 28 (1900).

[8] Siemens, *Ann. Physik*, **159**, 117 (1876); Saunders, *J. Phys. Chem.*, **4**, 423 (1900).

[9] Faraday, Expt. Res., 1833, 4th Series, 110; 1838, 12th Series, 426; Karsten, *Ann. Physik*, **71**, 239 (1847); Beetz, *ibid.*, **92**, 452 (1854); Bellati and Lussana, *Atti R. Inst. Veneto*, **5**, 1117 (1888); Streintz, *Ann. Physik*, 190, 171 (1902); Abt, *ibid.*, **62**, 474 (1897); Braun, *ibid.*, **153**, 556 (1874); **1**, 95 (1877); **4**, 476 (1878); **19**, 340 (1883); H. Meyer, *Beibl. Ann. Physik*, **5**, 199; *Ann. Physik*, **19**, 70 (1883); Matteucci, *Compt. rend.*, **40**, 541 (1855); **42**, 1133 (1856).

[10] *Ann. Physik*, 84, 1 (1851); cf. Urazov, *J. Russ. Phys. Chem. Soc.*, **51**, 311 (1919).

[11] Le Blanc and Kerschbaum, *Z. Elektrochem.*, **16**, 680 (1910). See also following sections.

[12] *Gilbert's Ann.*, **11**, 149 (1802); **22**, 14 (1806); for unipolar conduction of flames see J. J. Thomson, Conduction of Electricity through Gases, Cambridge, 1906, chapter 9, and Becker, *Jahrb. Radioakt. Elektronik*, **13**, 139 (1916).

noticed that if wires from a battery are introduced into a dry piece of soap no current passes. If the soap is connected to earth, current flows to earth from the negative wire only. The positive electrode becomes coated with an insulating layer of fatty acid. If the soap is moist, this is dissolved and current passes between the two wires.[1] The same phenomenon has been noticed in solutions, and whenever electrolysis leads to the formation of a sparingly soluble, poorly conducting, substance, which adheres to one of the electrodes, unipolar conduction occurs. This is applied in the aluminium rectifier,[2] which consists of a cell in which the anode is of aluminium and the electrolyte a solution of alkali phosphate, or borate, or a mixture of equivalent amounts of ammonium phosphate and borate. In this way an alternating is converted into a direct current.

Theory of Metallic Conduction: Metallic conduction differs from electrolytic conduction in the following particulars:[3] (1) There are no products of electrolysis; (2) there is no polarization: solid electrolytes, e.g., barium sulphate, exhibit a polarization of over one volt; (3) a substance which dissolves in water without decomposition to give a solution containing ions will probably conduct electrolytically in the solid state; (4) the resistance of a pure solid conductor (not a metal) has a minimum value at some temperature, whilst that of an electrolyte always diminishes with rise of temperature; (5) selective absorption and emission in the ultraviolet and infra-red are exhibited by electrolytic conductors, whilst in the case of metallic conductors, absorption and emission are continuous.

The conductivities of some elements (e.g., Si and Ti) and compounds have been studied by Koenigsberger and Schilling,[4] who found that a maximum conductivity was reached at a particular temperature in each case, which has no connection with transition temperature, and is attributed to electronic dissociation. The conclusion that metals contain not only free electrons and positive ions, but also negative ions, was reached on theoretical grounds by Jaffé,[5] the negative ions being regarded as associations of electrons with neutral

[1] The explanation given is due to Ohm.

[2] The rectifying action of aluminium was discovered by Buff, *Lieb. Ann.*, **102**, 265 (1857). See also B. K. Norden, *Z. Elektrochem.*, **6**, 159, 188 (1899); F. Fischer, *Z. physik. Chem.*, **48**, 177 (1904); Roloff and Siede, *Z. Elektrochem.*, **12**, 670 (1906); other metals (Mg, Ta, Nb, Sb, Bi, Zn, Cd) Günther-Schulze, *Ann. Physik*, **21**, 929 (1906) (bibliography); **22**, 543 (1907); **23**, 226; **24**, 43; **25**, 775 (1908); **26**, 372; **28**, 787 (1909); **34**, 657 (1911); *Z. Elektrochem.*, **18**, 326 (1912); *Ann. Physik*, **41**, 593 (1913); Baborovsky, *Z. Elektrochem.*, **11**, 465 (1905); Kistiakowsky, *ibid.*, **14**, 113 (1908); Foerster, *Elektrochemie wässriger Lösungen*, 1915, 376 ff.; bibliography, Günther-Schulze, *Jahrb. Radioakt. Elektronik*, **17**, 356 (1921); Winther, *Phys. Z.*, **14**, 823 (1913) (Mg, Al, Zn, Cd, Fe, Co, Ni, Pb, Sn, Sb, Bi, Cu, Ag, Pt, Au, Cr in KOH Aq.); Weiser, *J. Phys. Chem.*, **22**, 77 (1918).

[3] Koenigsberger, *Z. Elektrochem.*, **15**, 97 (1909); Friedrich and Sittig, *Z. anorg. Chem.*, **145**, 251 (1925).

[4] *Ann. Physik*, **32**, 179 (1910); summary of recent work on metallic conduction, Meissner, *Jahrb. Radioakt. Elektronik*, **17**, 229 (1920). Noyes, *Phys. Rev.*, **24**, 190 (1924); Siebel, Die Elektrizität in Metallen, 1922; Simon, *Z. Physik*, **27**, 157 (1924); Baedeker, Die elektrischen Erscheinungen in metallischen Leitern, 1911; Grüneisen, Handbuch der Physik (Geiger and Schell), vol. 13 (1928). For detailed account see Graetz, Elektrizität und Magnetismus, Leipzig, 1923, Vol 3, p. 597 (by Koenigsberger).

[5] *Physik. Z.*, **13**, 284 (1912); Kraus, *Phys. Rev.*, **4**, 159 (1914), concludes that only a small fraction of the molecules of liquid mercury are ionized.

molecules. On the theory of metallic conduction now accepted, free electrons are supposed to carry the current, the positive ions of the metal being immobile, or practically so. Other results lead to this theory, such as the work of Tolman and Stewart,[1] who calculated the ratio of the effective mass of the current carriers to the quantity of electricity carried. This ratio indicates that the carriers are free negative electrons. The thermoionic emission from metallic wires at high temperatures is also in good agreement with the electron theory.[2]

An early attempt at a theory of metallic conduction was made by Riecke,[3] who assumed also positive mobile particles. In the theory of Drude [4] the electrons in a metal are assumed to have the same mean kinetic energy as a gas molecule at the same temperature, and collisions between electrons and between electrons and metal atoms occur in the same way as those between gas molecules. The conduction is explained by the directive effect of the applied E.M.F. on the motion of the electrons, which preserve their random motion unchanged. On these assumptions, with certain simplifications,[5] the conductivity of a metal can be calculated.

Let e = electronic charge; N = number of electrons per unit volume; l = path traversed by an electron between two successive collisions; T = absolute temperature; m = mass of electron. If the electron is exposed to the electrical force E of the external field it will acquire velocity whilst moving in its free path. This increase will be zero at the beginning and $eE\tau/m$ at the end of the free path, where τ is the time in the free path. The mean increment of imparted velocity is thus $\Delta v = eE\tau/2m = eEl/2mv$, where $\tau = l/v$. The number of electrons moving per sec. through 1 cm.^{2} at right angles to the field is $N\Delta v$. The charge transported per sec. = current density, I. Thus:

$$I = N\Delta ve = Ne^2lE/2mv.$$

But $I = \kappa E$, where κ = conductivity. Hence:

$$\kappa = Ne^2l/2mv.$$

According to the simpler kinetic theory [6] as applied to a mass particle:

$$\frac{1}{2}mv^2 = \alpha T = \frac{3}{2}kT,$$

where k is Boltzmann's constant, hence:

$$\kappa = Ne^2l/2\sqrt{2\alpha mT} = Ne^2lv/6kT.$$

[1] *Phys. Rev.*, **8**, 97 (1916); **9**, 164 (1917).

[2] O. W. Richardson, The Emission of Electricity from Hot Bodies, London, 1916.

[3] *Ann. Physik*, **66**, 353, 545 (1898).

[4] *Ann. Physik*, **1**, 566 (1900); **3**, 369 (1900); **7**, 687 (1902); the same theory was put forward independently by J. J. Thomson, Rapports du Congrès Internat., Paris, **3**, 138.

[5] Cf. Reiche, Quantum Theory, 1922, pp. 160, 161.

[6] Cf. Jeans, Electricity and Magnetism, 1911, p. 306; the velocity component due to the impressed E.M.F. is very small compared with the value of v. The value of N has been calculated from optical and thermoelectric constants. It is then practically independent of temperature. Cf. Schenck, Physikalische Chemie der Metalle, Halle, 1909.

By a similar calculation the coefficient of thermal conductivity is found. The number of electrons which pass per sec. through 1 cm². at right angles to the x-axis under the influence of thermal agitation alone is $(1/6)Nv$, since one-third of the total number move parallel to this direction, half in one sense and half in the opposite sense. All the molecules of this class contained in an imaginary cylinder of length v, viz. $(1/6)Nv$, will just cross the area in 1 sec. The energy of each electron in the mean position is $(3/2)kT$ and hence the energies at distances l in front and behind will be:

$$\frac{3}{2}kT \pm \frac{\partial(3/2kT)}{\partial x}l.$$

The energy transport per sec. through unit area is thus:

$$\left(\frac{3}{2}kT - \frac{3}{2}k\frac{\partial T}{\partial x}l\right)\frac{1}{6}Nv - \left(\frac{3}{2}kT + \frac{3}{2}k\frac{\partial T}{\partial x}l\right)\frac{1}{6}Nv = -\tfrac{1}{2}Nlvk\frac{\partial T}{\partial x} = -\theta \cdot \frac{\partial T}{\partial x}$$

where θ is the coefficient of thermal conductivity. Thus:

$$\theta = \tfrac{1}{2}Nlvk;$$

hence

$$\theta/\kappa = 3k^2T/e^2 = T \times \text{const.}$$

which is the law of Wiedemann and Franz.[1]

Although experimental evidence on the whole supports Drude's theory, it is not free from difficulties. In the first place, the Wiedemann-Franz law is only approximate.[2] Eucken has considered the hypothesis of Koenigsberger that θ is composed of two parts: θ_m due to metallic conduction proper and θ_k due to " crystal or insulator conductivity." He finds that θ decreases strongly with decreasing grain-size in metals, but not in alloys, whilst κ remains practically constant. The experiments of Onnes at very low temperatures (see p. 616) show that a state of " super-conductivity " is reached before the absolute zero, when the resistance falls off more rapidly with temperature than according to the Wiedemann-Franz law. Again, the assumption of equipartition of energy between electrons and atoms would lead us to expect an additional $3/2 \cdot N_0 . k$, where N_0 is the number of electrons per gram atom, to the atomic heat of the metal, as compared with that of non-metals, which has never been observed. If we assume the number of electrons to be very small, the value of κ would be too

[1] *Ann. Physik*, **89**, 497 (1853); L. Lorenz, *ibid.*, **13**, 422, 582 (1881); Kirchhoff and Hausemann, *ibid.*, **13**, 406 (1881); Jaeger and Diesselhorst, *Abh. d. phys. tech. Reichsanstalt*, **3**, 269 (1900); Lees, *Phil. Trans.*, **208**, 381 (1907).

[2] Lees, *Phil. Trans.*, **208**, 381 (1907); Meissner, *Ann. Physik*, **47**, 1001 (1915); cf. Lorentz, *Proc. Amsterdam Acad.*, 1905; Koenigsberger, *Phys. Z.*, **8**, 273 (1907); Feussner, *Z. physik. Chem.*, **114**, 320 (1924); Eucken and Dittrich, *ibid.*, **111**, 431 (1924); **134**, 220 (1928); Eucken and Neumann, *ibid.*, **125**, 211 (1927); Meissner, Jahrb. f. Radioakt. u. Elektr., **17**, 241 (1921); Grüneisen and Goens, *Z. Physik*, **44**, 615 (1927); Grüneisen, *ibid.*, **46**, 151 (1928).

small, unless l is given improbably large values.[1] Another serious difficulty is that the assumption of equipartition would lead to the result that metals should radiate according to the law of Rayleigh, whereas they actually follow Planck's law, especially at low temperatures (cf. Chapter XVI). Attempts to remove this difficulty have been made by Wereide [2] and Nicholson.[3] The numbers of effective electrons in the atom have been calculated from the optical constants, and these come out very near whole numbers, but it has been generally recognized that the theory of equipartition requires modification.

Before discussing the newer theories brief mention may be made of the theory of Stark.[4] In this the valence electrons are assumed to be distributed symmetrically between the network of positive nuclei, lying on displacement surfaces in which they can move freely under an applied P.D. The number of transportable electrons is independent of temperature and (in a univalent metal) equal to the number of atoms. At any given temperature the resistance is determined by the thermal vibration of the electric valence fields. The thermal vibration vanishes at the absolute zero, and there is then no resistance. The small conductivities of non-metals is explained by the assumption that only a small number of electrons lie on displacement surfaces. Reduction in conductivity caused by foreign materials is assumed to be due to disturbance of the symmetry in the displacement surfaces, brought about by a relatively small number of foreign atoms, the electrons and atomic spheres of which are assumed to have a different spacial arrangement. The valence electrons bind together the positive spheres, i.e., determine the cohesion, and Stark [5] has put forward evidence in support of the connection between conductivity and plasticity.

Wagner,[6] by comparing the conductivities of metals in the solid and liquid states, finds ratios varying from 0.5 to 4.0. The number of electrons being assumed constant, the change must be due to changes of mobility.

Among the newer theories which attempt to get over the difficulties before mentioned are those of Nernst,[7] Onnes,[8] Lindemann,[9] J. J. Thomson,[10] Debye [11] and Bohr.[12] The formula of Lindemann shows that at high temperatures the specific resistance is proportional to the absolute temperature, whilst at low temperatures it falls off proportionally to $e^{-h\nu/2kT}$, where h is Planck's constant, ν is the frequency and k is Boltzmann's constant. The existence of zero resistance at low temperatures is thus covered. Wien [13] discards the theory of

[1] Cf. Reiche, "Quantum Theory," Eng. transl. 1922, pp. 63 ff.

[2] *Ann. Physik*, **55**, 589 (1918).

[3] *Phil. Mag.*, **22**, 245 (1911); Schuster, *ibid.*, **7**, 151 (1904).

[4] *Jahrb. Radioakt. Elektronik*, **9**, 188 (1912); based on his valence hypothesis, *ibid*, 124 (1908); Prinzipien der Atomdynamik, iii, 174 (1915).

[5] *Phys. Z.*, **13**, 585 (1912); cf. Credner, *Z. physik. Chem.*, **82**, 457 (1913).

[6] *Ann. Physik*, **33**, 1484 (1910).

[7] *Ber.*, **44**, 306 (1911).

[8] *Communications of Leyden Lab.*, 133 (1913).

[9] *Ber.*, **44**, 316 (1911).

[10] The Corpuscular Theory of Matter, 1907, Chap. IV.

[11] *Ann. Physik*, **33**, 441 (1910).

[12] *Diss.*, Copenhagen, 1911.

[13] *Ber.*, **46**, 184 (1913); cf. Keesom, *Phys. Z.*, **14**, 670 (1913).

equipartition of energy altogether and assumes that the electrons move with a velocity independent of temperature, and that N, the number of electrons per unit volume, is also independent of temperature. The variation of specific resistance is then determined only by the dependence of l, the mean free path, on temperature. Wien assumes a distribution of energy among the metal atoms in accordance with Debye's theory. This theory does not lead to a theory of heat conduction without fresh assumptions.

More recently Lindemann [1] and Haber [2] have made the assumption that the electrons in a metal, instead of being free to move like atoms of gas, are bound together in a space lattice, which moves through the metal as a rigid structure.

When a P.D. is applied, the electron space lattice [3] shifts as a whole through the atomic space lattice, the attraction of the more distant ions being counterbalanced by the repulsion of the inflowing electrons: "in other words," as Lindemann says, "the electron space lattice or crystal may be said to melt at one end and fresh layers may be said to freeze on at the other, when a current flows."

If a_0, the limit of the action of the repulsive force of the ions, is less than $\frac{1}{2}a$, where a is the distance between two atomic centers, the electron lattice may glide unimpeded through the atomic lattice, provided the atoms are at rest or their vibration does not exceed $\frac{1}{2}a - a_0$ in amplitude. The latter condition corresponds to the super-conductivity of Onnes in the region of the absolute zero. As the temperature increases the atomic amplitude increases and resistance is offered to the electron lattice.

Lindemann does not enter into any detailed calculation, but obtains the Wiedemann-Franz law. The absence of an electron term $(3/2)N_0kT$ in the energy of the metal is accounted for on Lindemann's theory. Other theories have been put forward by Herzfeld,[4] Hauer,[5] Grüneisen,[6] and others. Grüneisen finds that the specific resistance of pure metals at low temperatures is a universal function of $T/\beta\nu_m$, where β is the radiation constant $= h/k$, and ν_m a characteristic frequency. The ratio of resistivity to absolute temperature is proportional to the atomic heat of the metal. The variation of resistance with pressure confirms the view that the mean free path of the electrons is inversely proportional to the square of the amplitude of the vibrating atoms, which is in agreement with Lindemann's equations. Beckman [7] showed that in many

[1] *Phil. Mag.*, **29**, 127 (1915).

[2] *Ber.*, **52**, 506, 990 (1919); cf. Berelius, *Ann. Physik*, **57**, 278 (1918).

[3] Cf. Born and Kármán, *Phys. Z.*, **13**, 297 (1912); **14**, 15, 65 (1912); Born, *Ann. Physik*, **44**, 605 (1914); Dynamik der Kristallgitter, Berlin and Leipzig, 1915; Reiche, Quantum Theory, Eng. tr., 1922, p. 42; a difficulty in the lattice theory is that Ohm's law is obeyed down to the smallest applied P.D. Most theories suffer from the defect that they do not explain the production of Joule heat in the metal by the passage of the current.

[4] *Ann. Physik*, **41**, 27 (1913).

[5] *Ibid.*, **51**, 189 (1916).

[6] *Ber. Deut. phys. Ges.*, **15**, 186 (1913); **20**, 56 (1918).

[7] *Phys. Z.*, **16**, 59 (1915); **18**, 507 (1917): the result does not hold for Bi, Hg, Tl, Ta, Mo if p is the pressure and δr the resistance change, then $\delta r = ap + bp^2$, where a and b are constants, holds for many metals, *e.g.*, Zn, Fe, Pd, etc.

cases the change of resistance with pressure is in agreement with Grüneisen's views.

Benedicks [1] and Grüneisen [2] have shown that atomic conductance is a periodic function of atomic weight and decreases in value from the first to the eighth group in the periodic table. Streintz [3] found that between 18° and 100° the relation

$$\sqrt[3]{atomic\ volume} = \text{const.} \times dr/dT$$

holds for certain series of metals, such as Pd, Pt, Al, Ag, Au, Cd, Sn. The constant appears to vary from series to series, and to depend, to some extent, on the atomic volume of the metal.[4]

Bridgman [5] assumes that forces may act on the electron when in the act of passing from one atom to another in the metal, these forces depending on the amplitude of vibration of the atoms, whilst the electron in passing through the interior of the atom is not subject to any forces. There is, therefore, a possibility of transfer of energy to the electron only when it is crossing the " gap " between atoms, this gap producing resistance by interfering with the free path of the electron, or terminating it, as " collision " did in the older theory. At the absolute zero, with no amplitude of the atoms, there is no resistance to the motion of the electron, and the metal becomes superconducting. The difficulty of specific heats is got over and the correct temperature coefficient of resistance, $1/r \,.\, \partial r/\partial T = 1/T$, as well as the most important part of the pressure coefficient, are obtained. The classical equation: $\kappa = (e^2/2m)(Nl/v)$, is retained. The free path is supposed to be many atomic diameters, so that, M is small.

Metallic conduction has also been considered from the point of view of wave-mechanics. The Wiedemann-Franz-Lorenz [6] law is obtained (p. 612) with the factor $\pi^{2/3}$ instead of 3. An electron gas, with a Fermi energy partition law is assumed.

Effect of Temperature on Resistance of Metals: The relation between the specific resistance of a metal and temperature may be expressed by the formula:

$$r = a + bT + cT^2;$$

for small ranges of temperature the linear relation

$$r = a + bT$$

is sufficient, the coefficient having the value about $(1/r)dr/dT = 0.004$ (cf. coefficient of expansion of a gas), although for magnetic metals it is higher.

[1] *Jahrb. Radioakt. Elektronik*, **13**, 351 (1916).

[2] *Ber. Deut. phys. Ges.*, 20, 53 (1918). Cf. Simon, *Z. physik. Chem.*, **109**, 136 (1924).

[3] *Ann. Physik*, **33**, 436 (1910).

[4] Further papers on the conductivity of metals: Koenigsberger and Weiss, *Ann. de Phys.*, **35**, 1 (1911); J. J. Thomson, *Nature*, **96**, 494 (1915); *Phil. Mag.*, **43**, 721 (1922); **44**, 657 (1922); Bramley, *Phil. Mag.*, **46**, 1053 (1923); Höjendahl, *ibid.*, **48**, 349 (1924).

[5] *Phys. Rev.*, **17**, 161 (1921). Cf. Livens, *Proc. Camb. Phil. Soc.*, **22**, 555 (1925).

[6] Frenkel, *Z. Physik*, **29**, 214 (1924); *ibid.*, **47**, 819 (1928); Fermi, *ibid.*, **36**, 910 (1926); Pauli, *ibid.*, **41**, 87 (1927); Sommerfeld, *ibid.*, **47**, 1 (1928).

The coefficient increases with temperature, large changes being observed in the neighborhood of transition points and melting points. The coefficients for liquid metals are usually 1/5 those for solid.[1] Unlike the corresponding constants for gases, $(1/r)(dr/dT)_p$ and $(1/r)(dr/dT)_v$ are different.[2]

Lindeck [3] finds that (*specific resistance at a given temperature*) $\times$ (*temperature coefficient of resistance at the same temperature*) is constant for metals, even in presence of impurities (e.g., As in Cu).

At very low temperatures the resistance of some metals diminishes very rapidly with the temperature, and at 3° or 4° abs. the resistance may be zero, i.e., the metal is a perfect conductor. Our knowledge of the resistance of metals at very low temperature is due to the work of Kamerlingh Onnes and his co-workers at Leyden.[4] In the case of mercury, for example, at 13.9° abs. the resistance is 0.034 that of solid mercury at 273°. At 4.3° abs. it is 0.0013 times, and at 3° abs. less than 0.0001 times. Tin, thallium, indium and lead behave similarly. Such metals at these low temperatures are said to be in a "super-conducting" state. Most metals, such as gold, iron, silver, zinc, sodium, platinum, copper, and metals which tend to form solid solutions, do not become super-conducting.

An electric current induced in a ring of super-conducting metal by a magnet persisted for several hours without appreciable change. The effect of a magnetic field applied in the direction of the current is to reduce the conductivity in the case of superconducting metals at very low temperatures. On withdrawing the field the superconductivity returns. It is suggested that superconductivity is due to the formation of filaments of atoms along which the electrons pass more readily than between the spaces separating atoms [Haas, *J. de Physique*, 9, 265 (1928)].

In the case of alloys, it is found that compounds of a metal which becomes superconducting with one which does not, will become superconducting. At low temperatures the resistance of an alloy of gold and bismuth falls considerably. At 2.1° Abs. the resistance is 0.7 of its value at room temperature, whilst at a temperature 1/20° lower the resistance vanishes. It is suggested that superconductivity is connected with electron configuration, atomic weight and zero-point energy. The experiments show that combinations of two non-superconducting metals may become a superconductor [Haas, *Brit. Ass. Rep.*, 1928].

An apparatus for the measurement of resistance of metals at very high temperatures has been devised by Saldau.[5]

[1] Somerville, *Phys. Rev.*, **31**, 261 (1910); **33**, 77 (1911); Northrup, *T. Am. Electrochem. Soc.*, **20**, 185 (1911); *J. Franklin Inst.*, **177**, 287 (1914).

[2] Kraus, *Phys. Rev.*, **4**, 159 (1914); Somerville, *loc. cit.*

[3] *Ber Deut. phys. Ges.*, **13**, 65 (1911).

[4] *Proc. K. Akad. Wetensch. Amsterdam*, **13**, 1274 (1911); **14**, 818 (1912); **15**, 1406 (1913); **16**, 113, 673 (1913); **17**, 508 (1914); **26**, 504 (1923); see also Clay, *Jahrb. Radioakt. Elektronik*, **8**, 383 (1911); **12**, 259 (1915); Crommelin, *Phys. Z.*, **21**, 274, 300, 331 (1920); *Chem. Weekblad*, **16**, 640 (1919); Meisoner, *Z. Physik*, **38**, 647 (1926); McLennan and Niven, *Phil. Mag.*, **4**, 386 (1927); McLennan, Niven and Wilhelm, *ibid.*, **6**, 666, 672, 678, (1928)—Cd, Pb alloy superconducting up to 5 per cent Cd.

[5] *Iron and Steel Inst. Carnegie Schol. Mem.*, **7**, 195 (1916).

Conductivity of Alloys: The electrical conductivity of alloys [1] is characteristic. Each component contributes to it, so that if an alloy is purely a mechanical mixture its conductivity is an additive property of the volume percentages of the components. Isomorphous mixtures have a conductivity which is always less than that calculated from the mixture law, and is diminished by addition of foreign substances. The formation of a solid solution is accompanied by considerable increase in the resistance of the alloy, and this increases also with increase of concentration.[2] When the components form a compound this possesses a peculiar and characteristic conductivity which is relatively high, and is diminished by additions of foreign substances. The temperature coefficients of intermetallic compounds differ but little from the normal value (0.004) for pure metals.[3] In the case of solid solutions the temperature coefficients are much lower.[4]

Lord Rayleigh [5] showed that the application of an E.M.F. to an alloy should call into play opposing thermoelectric forces, due to the Peltier effects at the numerous boundaries between the different metals, and, according to Liebenow,[6] this is the reason why the conductivity of alloys consisting of different kinds of molecules is always less than according to the mixture rule. From this assumption the properties of alloys can be deduced,[7] except those of solid solutions, when the explanation of Rayleigh seems to break down.[8]

Matthiessen [9] put forward the general law that the conductivity of a binary alloy may be represented by the equation

$$\kappa_m/\kappa = P_m/P,$$

where κ and κ_m are the observed conductivity and that calculated from the mixture rule, respectively, and P and P_m are the corresponding temperature coefficients. Since $P_m = 100(\kappa_0 - \kappa_{100})/\kappa_0$ for all metals is equal to 29 ± 2,

[1] Desch, Metallography, London, 1922, 253; Guertler, *Jahrb. Radioakt. Elektronik*, **5**, 17 (1908); Le Chatelier, *Revue générale des sciences*, **6**, 531 (1895); Contribution à l'étude des alliages, Paris, 1901, 446; Skaupy, *Ber. Deut. phys. Ges.*, **18**, 252 (1916); Schenck, *Ann. Physik*, **32**, 261 (1910); for evidence of electrolytic conduction see Kremann, etc., *Monat.*, **44**, 401 (1924) and many later papers.

[2] Pushin and Maximenko, *J. Russ. Phys. Chem. Soc.*, **41**, 500 (1909); Chem. Abs., **5**, 819 (1911); Pushin and Dishler, *ibid.*, **44**, 125 (1912); Chem. Abs., **6**, 1587 (1912); N. I. Stepanoff, *ibid.*, **44**, 910 (1912); Chem. Abs., **6**, 2187 (1912); Kurnakoff and Schemtchuschny, *ibid.*, **39**, 211 (1907); Norbury, *Trans. Faraday Soc.*, **16**, 570 (1920).

[3] Pushin and Dishler, *loc. cit.* Alloys of brittle and easily oxidized metals can be suitably cast according to the method of N. J. Stepanoff, *Z. anorg. Chem.*, **60**, 209 (1908); *J. Russ. Phys. Chem. Soc.*, **40**, 1448 (1908); Chem. Abs., **3**, 773 (1909). On solid solutions see also Guertler, *Z. anorg. Chem.*, **51**, 397 (1906).

[4] N. I. Stepanoff, *loc. cit.*

[5] *Electrician*, **37**, 277 (1896); *Nature*, **54**, 154 (1896); *Collected Papers*, iv, 232; experimental demonstration, Pushin and Maximenko, *loc. cit.*, Willows, *Phil. Mag.*, **12**, 604 (1906) Cuy, *Phil. Mag.*, **49**, 753 (1924).

[6] *Z. Elektrochem.*, **4**, 201 (1897); Der elektrische Widerstand der Metalle, Halle, 1908.

[7] Nernst, Theoret. Chem., 8–10 Aufl., p. 471.

[8] Desch, Metallography, 1922, 255; Schenck, *Metallurgie*, **4**, 161 (1907); *Physik. Z.*, **8**, 239 (1907); Guertler, *Z. anorg. Chem.*, **54**, 58 (1907).

[9] *Ann. Physik*, **112**, 353 (1861).

we can write the law $\kappa_m P/\kappa = 29 \pm 2$. For alloys free from mixed crystals, $\kappa_m = \kappa$, and the rule becomes $P = 29 \pm 2$.

The correctness of Matthiessen's law has been demonstrated by other experimenters.[1] The law has been modified by Guertler,[2] who states that the conductivity of a binary alloy and its temperature coefficient are proportional, even when mixed crystals and compounds are present. Guertler and Schulze [3] state the law in the form that the absolute increase in resistance on raising the temperature of a binary alloy from 0° to 100° is independent of the increase of resistance brought about by the presence of mixed crystals and has the same value as that calculated from the increase of resistance of the pure components when raised through the same temperature interval: $dr_m/dt = dr/dt$. This is confirmed by experiment. Hence $r_m = r(T) + z$, where $r(T)$ is the specific resistance of a pure metal, r_m that of the metal containing an impurity and z the resistance due to the impurity, which remains constant in value at all temperatures. This has been confirmed by experiment and holds at low temperatures, when $r(T)$ becomes small compared with z. [Nernst, *Berlin Ber.*, 1911, p. 306; Schimank, *Ann. Physik*, 45, 706 (1914).] Nernst has used this result to find the temperature coefficient of resistance of a platinum wire for use as a resistance thermometer, by comparison with the resistance of another wire for which the temperature coefficient is known over a range of temperatures. Let $r/r_0 = R$, r_0 being the resistance at 0° C. Then for the two wires $R_2 = (R_1 - \alpha)/(1 - \alpha)$, α being a constant. Thus only one empirical constant is required. Callendar's method requires two constants [Henning, Temperaturmessung, 1915, p. 103].

The constitution of binary alloys may be deduced from conductivity measurements.[4] The following are the most important results: (1) Alloys for which the electrical conductivity is a linear function of the volume composition have components not miscible in the solid state. (2) Alloys forming a complete series of solid solutions (e.g., Ag–Au) have a continuous conductivity curve (plotted against volume concentration). (3) The components of some alloys exhibit only limited miscibility: in this case the last statement holds for that part of the curve between the pure metals and the saturated solid solutions, while the first statement holds for that part of the curve between the compositions of the saturated solid solutions. (4) If two metals form m compounds, the conductivity-concentration diagram can be divided into $m + 1$ single binary diagrams, and from the shape of the curves information on the existence of compounds may be obtained. (5) The electrical conductivity of a system can never exceed the values on the straight line joining the conductivities of the

[1] Matthiessen and Vogt, *Ann. Physik*, **122**, 19 (1864); Dewar and Fleming, *Phil. Mag.*, **34**, 326 (1892); **36**, 271 (1893); Reichardt, *Ann. Physik*, **6**, 832 (1901), etc. References in Guertler, *Z. anorg. Chem.*, **54**, 72 (1907); *Z. Elektrochem.*, **18**, 601 (1912); Graetz, *Handb. d. Elektrizität*, vol. iii, p. 631 (1923); Lienipt, *Z. Physik*, **41**, 867 (1927).

[2] *Loc. cit.*

[3] *Z. physik. Chem.*, **104**, 90 (1923).

[4] Guertler, *Z. anorg. Chem.*, **51**, 397 (1906); **54**, 58 (1907); *Z. Elektrochem.*, **18**, 601 (1912) *J. Inst. Metals*, **6**, 135 (1911).

pure components. (6) A sharp point on the curve always indicates the presence of a chemical compound, but the converse does not hold, although Liebenow considers that it does.

The constitution of alloys may also be elucidated from a consideration of the temperature coefficients of conductivity. Alloys containing solid solutions have a value of P which falls rapidly from the value for pure metals, and the curves connecting P with the composition of the alloys show in many cases breaks corresponding with those in the miscibility of the metals. The resistance of solid solutions is supposed to persist even at the absolute zero, whereas that of pure metals tends to vanish at $T = 0$. The values of the Wiedemann-Franz constant θ/κ are smaller when solid solutions are formed than with pure metals.[1] When solid solutions are not formed, it has the same value as for pure metals.

Conductivity of Liquid Alloys and Amalgams: Little work has appeared on the conductivities of liquid alloys.[2] Some experiments have been made by Bornemann and Müller,[3] glass or quartz vessels being used. Liquid alloys of sodium and potassium give a curve typical of a continuous series of solid solutions with a well-marked minimum. There is no indication of the compound Na_2K, but NaK appears to exist. Liquid alloys of lead and tin exhibit a conductivity which varies linearly with composition. The curve for liquid alloys of copper and nickel is continuous with a distinct minimum; that for copper and antimony shows a break at Cu_3Sb,[4] which is more strongly marked in the curve of temperature coefficients. The influence of added metal on the conductivity of a liquid metal is quite independent of the conductivity of the added metal. The determining factor seems to be tendency to compound formation. The alkali metals, having a strong tendency to combination, always lower the conductivity of a liquid metal to which they are added, whilst indifferent metals may either raise or lower it.

The conductivity of mercury is lowered by addition of alkali metal, but raised by addition of other metals.[5] The low temperature coefficient of mercury [6] has been attributed to the presence of two or more different kinds of molecules giving it the properties of an alloy. The addition of alkali metals (except lithium) which form compounds with mercury, and increase the number of complex molecules, lowers its conductivity in accordance with this view, whilst indifferent metals (lithium, calcium, strontium), which dissolve in the monatomic form, raise it.[7] The effect increases with temperature. The

[1] Schulze, *Ann. Physik*, 9, 555 (1902); Höjendahl, *Phil. Mag.*, 48, 349 (1924); Borelius, *Ann. Physik*, 77, 109 (1924)—N and v different for the different constituents of an alloy (see p. 611).

[2] Cf. Graetz, *Handb. der Elektrisität*, vol. iii, p. 652 (1923).

[3] *Metallurgie*, 7, 396 (1910); Bornemann and Wagenmann, *Ferrum*, 11, 276, 289, 330, (1914); Müller, *Metallurgie*, 7, 730, 755 (1910).

[4] Bornemann and Rauschenplat, Metallurgie, 9, 473, 505 (1912).

[5] Bornemann and Müller, Metallurgie, 7, 396 (1910).

[6] About 0.001; Liebenow, Die elektrische Widerstand der Metalle.

[7] Fenninger, Diss., Freiburg, 1914; Lewis, Adams and Lamman, *J. Am. Chem. Soc.*, 37, 2656 (1915), attribute the lowering in conductivity to a reduction in the average mobility of the electrons. Cf. Kremann and co-workers, *Monatsh.*, 44, 401, 383 (1924).

conductivity curve for amalgams exhibits a maximum corresponding with $NaHg_2$ [1] and one corresponding with KHg. Metals dissolved in mercury are assumed by Skaupy [2] to be ionized to a considerable extent. Lewis, Adams, and Lamman [3] found transfer of alkali metal from kathode to anode in the electrolysis of sodium amalgams, and assumed that the sodium atoms form nuclei on which large aggregates of mercury atoms collect, the whole aggregate being less easily penetrated by electrons than free mercury atoms.

The Conductivity of Solid Salts and Glass: Some experiments on the conductivities of solid sulphides were made by Faraday.[4] In the case of silver and lead halides, no sudden change of conductivity occurs on fusion.[5] In other cases sudden changes occur on fusion,[6] or when the substance passes through a transition point.

Experiments on the conductivity of glass [7] show that the sodium ions move; they may be replaced by other ions, e.g., silver, to a limited extent; with larger amounts cracking occurs.

The conductivities of mixed oxides were investigated by Reynolds,[8] who used principally zirconium and cobalt oxides, with various added oxides. With increasing concentration of the latter the conductivity passes through a maximum. The true electrolytic character of the conduction in such mixtures was established by Nernst [9] and Bose.[10] The Nernst lamp [11] makes use of these

[1] Cf. Hine, *J. Am. Chem. Soc.*, **39**, 879 (1917), who finds that the conductance of sodium amalgam passes through a minimum. Cf. Vanstone, *Trans. Farad. Soc.* 9, 291 (1914).

[2] *Ber. Deut. physikal. Ges.*, 18, 252 (1916); Williams, *Phil. Mag.*, 589 (1925); Edwards, *bid.*, 2, 1 (1926); Jones and Jones, *ibid.*, 2, 176 (1927); Johns and Evans, *ibid.*, 5, 271 (1928).

[3] *J. Am. Chem. Soc.*, **37**, 2656 (1915).

[4] *Phil. Trans.*, **123**, 507 (1833); Expt. Res., 4th Series, 110 ff., 7th Series, 201; Braune, *Z. Elektrochem.*, **31**, 576 (1925).

[5] E. Wiedemann, *Ann. Physik*, **154**, 318 (1875); W. Kohlrausch, *ibid.*, **17**, 642 (1882); Ayrton, *Phil. Mag.*, **6**, 132 (1878); L. Poincaré, *Ann. Chim. Phys.*, **21**, 289 (1890); Graetz, *Ann. Physik*, **40**, 18 (1890); Lapschin and Tichanowitsch, *Bull. Acad. Petersb.*, vol. 4 (1861); Tubandt, *Nernst Festschrift*, p. 446 (1912); Tubandt and Lorenz, *Z. physik. Chem.*, **89**, 513 (1914). Cf. Frers, *Ber.*, **57**, 1693 (1924).

[6] T. Andrews, *Proc. Roy. Soc. Edin.*, **13**, 275 (1884); W. Kohlrausch, *Ann. Physik*, **17**, 642 (1882) (AgI); S. P. Thompson, *Nature*, **24**, 469 (1881) ($HgCu_2I_4$); Beetz, *Ann. Physik*, **92**, 452 (1854); *ibid.*, *Jubelband*, 23 (1874) (HgI_2); Lorenz, *Elektrolyse geschmol. Salze*, ii, 241 ff.; Gros, *Sitz. ber. Preuss. Akad.*, 500 (1877).

[7] Warburg, *Ann. Physik*, **21**, 622 (1884); T. Gray, A. Gray, and Dobbie, *Proc. Roy. Soc.*, **36**, 488 (1884); F. Tegetmeier, *Ann. Physik*, **41**, 18 (1890); Kraus and Darby, *J. Am. Chem. Soc.*, **44**, 2783 (1922); LeBlanc and Kerschbaum, *Z. physik. Chem.*, **72**, 468 (1910); Speranski, *J. Russ. Phys. Chem. Soc.*, **47**, 52 (1915); Pirani and Lax, *Z. techn. Physik*, **3**, 232 (1922); Pirani and Siemens, *Z. Elektrochem.*, **15**, 969 (1909); Haber, Thermodynamics, Eng. tr. 1908, 318; Winkelmann's Physik, IV, i, 452; Lorenz, Elektrolyse geschm. Salze, ii, 229ff.; Schönborn, *Z. Physik*, **22**, 305 (1924); Hurd, Engel and Vernon, *J. Am. Chem. Soc.*, **49**, 447 (1927); Schumacher, *ibid.*, **46**, 1772 (1924); Rebleck and Ferguson, *ibid.*, **46**, 1991 (1924)—gas evolved from absorbed water; Poole, *Phil. Mag.*, **42**, 488 (1921)—Ohm's law not followed; Bush and Connell, *J. Franklin Inst.*, **194**, 231 (1922).

[8] *Diss.*, Göttingen, 1902.

[9] *Z. Elektrochem.*, **6**, 41 (1899).

[10] *Ann. Physik*, **9**, 164 (1902).

[11] *Elektrotechn. Z.*, **19**, 272 (1898); **22**, 400, 620 (1901); **24**, 281, 442 (1903); **25**, 610, 751 (1904). Zirconia and thoria, with rare earths, are used. See also Zimmerman, *Trans. Am. Electrochem. Soc.*, **7**, 79 (1905), who finds electrolysis takes place in Nernst filaments.

results. Graetz[1] found that the conductivity of solid salts is increased by compression. Arrhenius[2] found the conductivities of silver chloride and bromide to be affected by light. Brown[3] found the conductivity of solid copper ferrocyanide to take place without polarization. A very complete investigation of the conductivities of solid salts was made by J. Rosenthal.[4] He cast or pressed the substance into sticks, bored holes in these, covered the insides with graphite, and inserted platinum wires which were fixed in place with Rose's metal. The results, although numerous, were more or less qualitative. In some cases the crystalline form conducted better than the amorphous, sometimes both equally well. The conductivity of lead chloride changed with time, probably owing to change of modification. Some salts conducted only at higher temperatures (e.g., $K_2Cr_2O_7$ above 310°). Foussereau[5] measured the conductivities at various temperatures, and found that the specific resistances could be represented by equations of the form:

$$\log r = a - bt + ct^2,$$

where t = temperature. Rasch and Hinrichsen[6] and Königsberger[7] independently proposed the formula:

$$\log \kappa = a + b/T$$

where a and b are constants. Phipps, Lansing and Cooke[8] adopted Königsberger's suggestion that this is of the form

$$\log \kappa = -q/RT + c^1$$

where q is a *heat of liberation* of a gram ion in the crystal lattice, or the work necessary to produce a mol. of gaseous ions in the interior of the crystal, closely related to the characteristic quantum frequency of the crystal. Vaillant[9] finds that the formula $\log \kappa = a - bt$ gives much better results than $\log \kappa = a + b/T$. The conduction is attended by movement of ions, although this is extremely slow.[10]

The following method is described for the measurement.[11] The powder is

[1] *Ann. Physik*, **29**, 314 (1886).
[2] *Wien. Akad. Ber.*, **96**, 831 (1887); *Beibl. Ann. Physik*, **12**, 119 (1888).
[3] *Phil. Mag.*, **33**, 82 (1891).
[4] *Ann. Physik.*, **43**, 700 (1891).
[5] *Ann. Chim. Phys.*, **5**, 241, 317 (1885).
[6] *Z. Elektrochem.*, **14**, 41 (1908).
[7] *Physik. Z.*, **8**, 833 (1907).
[8] *J. Am. Chem. Soc.*, **48**, 112 (1926).
[9] *Compt. rend.*, **182**, 1335 (1926).
[10] von Hevesy, *Z. Physik.*, **2**, 148 (1920); **10**, 80 (1922); *Z. Elektrochem.*, **34**, 463 (1928); Smekal, *ibid.*, 472; von Seelen, *Z. Physik*, **29**, 125 (1924); Geiger and Scheel's *Handb. d. Physik*, **13**, 263 (1928).
[11] Benrath, *Z. physik. Chem.*, **64**, 693 (1908); von Rautenfeldt, *Ann. Physik*, **72**, 617 (1913); **75**, 848 (1924); Phipps, Lansing and Cooke, *J. Am. Chem. Soc.*, **48**, 112 (1928); Gingold, *Z. Physik*, **50**, **633** (1928); Vaillant, *Compt. rend.*, **179**, 530 (1924); **180**, 206 (1924); Fischer, *Z. Elektrochem.*, **32**, 136, 538 (1926); *ibid.*, **33**, 170, 172, 571 (1927); Tubandt, Reinhold and

strongly compressed into small cylinders, the ends of which are covered with a thin layer of graphite. Ketzer [1] finds that the conductivity may change as much as 12 per cent according to the pressure used in making the cylinders. Connection is made with the circuit by means of platinum plates pressed firmly against the ends. Tubandt [2] finds that the interposition of a cylinder of cubic silver iodide between the kathode and cylinder of salt is an improvement when direct current is used. It prevents possible short circuiting owing to the formation of a metal bridge, which is one of the chief difficulties. Kohlrausch's method is used for the measurement. In the case of potassium, sodium and silver nitrates the resistance of the crystalline substance is more than 10,000 times that of the fused, and the relation is:

$$\log \kappa = a + bt.$$

The conductivity of solid solutions always exceeds that of the components, the reverse being the case for metals. Similar results were found for silver, potassium and sodium chlorides, and potassium chromate,[3] but in the binary system AgCl–KCl the conductivity is the sum of those of the constituents, since these are not miscible. The sudden changes at melting or transition temperatures are proposed in the measurement of these temperatures.[4] The conductivity isotherms used for alloys do not represent the results with solid mixtures of salts.[5]

Haber and Zawadzki [6] found that when solid compressed silver salts (halides, sulphate) are electrolyzed between silver plates, polarization occurs, which is greater the lower the temperature and increases when the salts are kept compressed for some time. They suggested that the current is transported by electrons, with simultaneous formation of oxidizing materials such as free halogens or silver persulphate, which then attack the anode.

The conductivity of [7] silver iodide powder falls rapidly at first, then reaches a limiting value, rising, at first rapidly and then slowly, to its initial value when the circuit is broken. The conductivity of barium sulphide is constant for the solid, but rises when the substance is powdered. The conductivity of powdered molybdenite rises on the application of an E.M.F. Ohm's law is not obeyed for powders except in the case of zinc perborate. The conductivity of a powder falls in a vacuum, at first rapidly, then slowly.

Jost, *Z. physik. Chem.*, **129**, 69 (1927); Tubandt, Rindtorff and Jost, *Z. anorg. Chem.*, **165**, 195 (1927).

[1] Ketzer, *Z. Elektrochem.*, **26**, 77 (1920).

[2] Tubandt, *Z. anorg. Chem.*, **115**, 103 (1921). Cf. Tubandt and Eggert, *ibid.*, **110**, 196 (1920).

[3] Benrath and Wainoff, *Z. physik. Chem.*, **77**, 257 (1911). On the conductivity of crystals see Doelter, *Monatsh.*, **31**, 498 (1910).

[4] Benrath, *Z. physik. Chem.*, **64**, 693 (1908); cf. Tubandt and Lorenz, *ibid.*, **87**, 513 (1914).

[5] Benrath and Tesche, *Z. physik. Chem.*, **96**, 474 (1920).

[6] *Z. physik. Chem.*, **78**, 228 (1912).

[7] Goddard, *Phys. Rev.*, **28**, 405 (1909); Bruni and Scarpa, *Atti. R. Accad. Lincei*, **22**, 438 (1913); Tuband and Lorenz, *Z. physik. Chem.*, **87**, 560 (1914); Cichochi, *Compt. rend.*, **187**, 287 (1928); Jakubsohn and Rabinovitsch, *Z. physik. Chem.*, **116**, 359 (1925)—salt hydrates.

The conductivity of solid calcium sulphide increases rapidly with the temperature and also under the influence of light up to a point,[1] the curve showing an acute maximum, from which it descends to zero as the temperature is raised still higher. The phenomenon is probably connected with the state of phosphorescence.

Sandonnini [2] found that the conductivity isotherms of the system $PbCl_2$–$PbBr_2$ all show a minimum corresponding approximately to equimolecular proportions. In the system AgCl-AgBr, the conductivities of mixtures containing between 0 and 70 molar per cent of bromide are less, and those of the remaining mixtures slightly greater than the values calculated by the law of mixtures. The conductivities of solidified mixtures of salts are less than those calculated additively when they form perfectly homogeneous solid solutions with melting points intermediate between those of their components. Benrath (above) found with mechanical mixtures that the additive value is always exceeded, the only apparent cause for which lies in the gradual diminution of internal friction, because the maximum is observed at a point where the conductivity isotherm lies close to the eutectic point. The large increases in conductivity found by Fritsch [3] on mixing halides of lead and mercury with those of alkali metals, when solid solutions were supposed to be formed, do not occur in the complete absence of moisture and if the mixture is not overheated. LeBlanc,[4] who measured the conductivities at 18° of lead, potassium and barium fluorides and mixtures of these, found that the conductivity of lead fluoride is doubled by the addition of 5 per cent of barium fluoride, and becomes five times as great by the addition of 5 per cent of potassium fluoride.

Usually positive or negative ions only are the carriers in solid salts: the conduction is unipolar. Tubandt [5] finds that with solid silver iodide, bromide, anld chloride the current is carried entirely by the silver ion. Faraday's law hods to within 1 per cent with these salts and silver nitrate.[6] A layer of silver iodide was interposed between the salt and kathode. In the case of silver iodide the velocity of the silver ion in the solid was 0.55×10^{-3} cm./sec. per volt per cm. at 145° C., approximately the same as its value in aqueous solution at 18°, and double this value at 552°. In the case of lead chloride the current

[1] Vaillant, *Compt. rend.*, **154**, 867 (1912); **171**, 1380 (1920); cf. Pélabon, *ibid.*, **173**, 142, 295 (1921) (thallous sulphide and selenide); **152**, 1302 (1911) (antimony selenides); on the unipolar conduction of stibnite see Martin, *Phys. Z.*, **12**, 41 (1911). The conductivity of finely divided salts is a function of the size of the particles; Fink, *J. Phys. Chem.*, **21**, 32 (1917).

[2] *Atti R. Accad. Lincei*, (v), **24**, i, 842 (1915); *Gazzetta*, **50**, i, 289 (1920); Ketzer, *Z. Elektrochem.*, **26**, 77 (1920), finds that the conductivity of solid lead chloride is largely influenced by previous treatment, and LeBlanc, *ibid.*, **18**, 549 (1912), finds the same with lead fluoride, potassium fluoride and barium fluoride.

[3] *Ann. Physik.*, **60**, 300 (1897).

[4] *Z. Elektrochem.*, **18**, 549 (1912); see description of apparatus.

[5] *Z. anorg. Chem.*, **115**, 105 (1921); LeBlanc and Kröger, *Z. Elektrochem.*, **30**, 253 (1924); **31**, 359 (1925); Schmidt, *ibid.*, **30**, 440 (1924); Frers, *Ber.*, **57**, 1693 (1924); Tubandt and Reinhold, *Z. Elektrochem.*, **31**, 84 (1925); Friederich, *ibid.*, **32**, 576 (1926); Friederich and Meyer, *ibid.*, 566; Frenkel, *Z. Physik*, **26**, 137 (1924); **35**, 652 (1926); Braunbeck, *ibid.*, **44**, 684 (1927).

[6] Cf. Tubandt and Eggert, *Z. anorg. Chem.*, **110**, 196 (1920).

is carried by the chloride ion, and in lead fluoride by the fluoribe ion. Above 180° silver sulphide is a true electrolytic conductor, the silver ion carrying the current and moving with a velocity of 0.11 cm./sec.[4] Below 180° it changes into another form, which shows metallic as well as electrolytic conductivity. The cubic form of cuprous sulphide [1] is a pure electrolytic conductor, the metal ions carrying the current. Insulating crystals may be divided into two classes: (i) the calcite type, (ii) the quartz type. When a P.D. is applied to the crystal and then removed, a polarisation (which may attain very high values) remains. In the case of calcite the polarization is removed by grinding away a thin layer (0.01 mm.) on the kathode side but is unaffected by removing a layer from the anode side. Hence it is supposed that the polarization is due to a space-charge due to the calcium ions which have moved towards the kathode but have not been discharged. In the case of quartz, the polarization is not removed by grinding away even thick layers at the anode and kathode sides, but it is reduced, hence it is assumed that in this case the polarization is due to the separation of both positive and negative ions, which are further shown to have different mobilities. In the quartz crystal there are very few ions but these possess high mobilities. [Joffé, *Ann. Physik*, 72, 461 (1923); 4th Solvay Congress, 5, 13 (1924); The Physics of Crystals, 1928.]

The question as to whether a perfect crystal, with an undisturbed lattice, can show any conductivity at all, has been considered. [See von Hevesy, Geiger and Scheel's Handbuch der Physik, 13, 286 f. (1928).] The conductivity of a single crystal is normally much smaller than that of a crystal aggregate and it is suggested that small quantities of other salts present as impurities may loosen the lattice and increase the conductivity. Ultramicroscopic pores may also exist in crystals, through which conduction occurs.

Electrolysis of Fused Salts: The conductivity of fused salts is more difficult to measure than that of solutions, and the results are not easy to interpret.

Davy in 1801 found that fused nitre, caustic potash and soda are conducting (Faraday, *Expt. Res.*, 5th series, 1833, p. 133). Faraday (*loc. cit.*) investigated many fused salts and found that they were decomposed according to the law of electrochemical equivalents. The problem was taken up by Matteucci [2] and by Braun,[3] both of whom paid careful attention to polarization, since direct current was used. Braun was led to a speculation as to the state of salts in solution which approaches the ionic theory.[4] The application of alternating current was made by Kohlrausch.[5] Foussereau [6] determined the specific conductivities of a number of fused salts by various methods, paying

[1] The α-form of Ag_2S follows Faraday's law exactly; Tubandt, Eggert and Schibbe, *Z. anorg. Chem.*, **117**, 1 (1921). Mixtures of Ag_2S and Ag do not follow the law (Tubandt and Eggert, *ibid.*, **117**, 48) until all the free silver has migrated to the kathode and pure Ag_2S remains. Tubandt and Reinhold, *Z. anorg. Chem.*, **160**, 223 (1927); Tuband and Haedicke, *ibid.*, 299.

[2] *Ann. de Chim.*, **15**, 498 (1845).

[3] *Ann. Physik*, **154**, 161 (1875).

[4] Lorenz, Elektrolyse geschm. Salze, ii, 194.

[5] *Ann. Physik*, **17**, 642 (1882).

[6] *Ann. Chim. Phys.*, **5**, 241, 317 (1885).

careful attention to polarization, the effect of temperature,[1] and viscosity. Bouty and Poincaré[2] used the method which had been applied by Bouty to solutions (see later) and observed conduction on the walls of the glass cell at high temperatures. They found that the conductivity of mixtures of similar salts was additive. Poincaré[3] then carried out an extensive investigation on the conductivities of fused salts at various temperatures. The conductivity increases with temperature more rapidly than linear proportionality, but obeyed the formula

$$\kappa = e^{\alpha+\beta t+\gamma t^2}.$$

The ratio of the molecular conductivities of sodium and potassium salts was independent of the anion. An extensive series of measurements was also made by Graetz.[4] The subject has, however, been principally advanced by the work of Richard Lorenz and his co-workers.[5]

The principal difference from the case of solutions is that, whereas in the latter case mixtures of solute and practically non-conducting solvent are involved, in the case of fused salts either only one substance is present or the components are conductors of the same class. In spite of this great difference the ions deposited are the same in both cases, and Faraday's law is obeyed, with the value of F = 96,500 coulombs (see "Faraday's Laws"). In the deposition of silver the accuracy is 0.005 per cent up to 260°, and 0.9 per cent up to 640°; with lead the accuracy is about 1 per cent up to 1050°.[6]

The conductivity is mainly conditioned by the temperature. Polarization is observed, and cells of the Daniell type, as well as those with liquid junctions, may be set up with fused salts,[7] the E.M.F.'s being of the same order as in aqueous solutions. Freezing point measurements indicate that complex salts

[1] Cf. Biltz, *Z. anorg. Chem.*, **133**, 306 (1924).

[2] *Ann. Chim. Phys.*, **17**, 52 (1889).

[3] *Ann. Chim. Phys.*, **21**, 289 (1890); *Compt. rend.*, **108**, 138 (1889); **110**, 339 (1889).

[4] *Ann. Physik*, **40**, 18 (1890).

[5] Elektrolyse geschmolzener Salze, 3 parts, Halle, 1905–6; *Z. physik. Chem.*, **70**, 230 (1910); the following account is mainly derived from these sources, except for later work. Lorenz and Kalmus, *Z. physik. Chem.*, **59**, 17 (1907); Schultze, *Z. anorg. Chem.*, **20**, 323, 333 (1899)—who realized the great influence of traces of moisture; Helfenstein, *ibid.*, **23**, 255 (1900); Lorenz, *ibid.*, **23**, 97 (1900); Grünauer, *ibid.*, **39**, 389, 404 (1904) (very detailed); Quincke, *Ann. Physik*, **36**, 270 (1889); Aten, *Z. physik. Chem.*, **73**, 578 (1910); **78**, 1 (1912); Arndt, Physikalisch-Chemische Technik, p. 592; *Ber.*, **40**, 2937 (1907); cf. Lorenz, *ibid.*, 3308, 4378; Jaeger and Kapma, *Z. anorg. Chem.*, **113**, 27 (1920); Appelberg, *ibid.*, **36**, 36 (1903); Auerbach, *ibid.*, **28**, 1 (1901); Lorenz, *Z. Elektrochem.*, **30**, 371 (1924); Voigt and Beltz, *Z. anorg. Chem.*, **133**, 277 (1924); Wartenburg, *Z. Elektrochem.*, **32**, 330 (1926); **33**, 526 (1927); Arndt, *ibid.*, **33**, 236 (1927); Schischkin, *ibid.*, 83; Arndt and Ploetz, *Z. physik. Chem.*, **110**, 237 (1924); Biltz and Klemm, *ibid.*, 318; Arndt and Kalass, *Z. Elektrochem.*, **30**, 12 (1924); von Hevesy, *ibid.*, **34**, 463 (1928); Walden, Ulich and Birr, *Z. physik. Chem.*, **131**, 1, 21, 31 (1927).

[6] Cf. Bruni and Scarpa, *Atti R. Accad. Lincei*, **22**, i, 438 (1913); Tubandt and Lorenz, *Z. physik. Chem.*, **87**, 513 (1914).

[7] Lorenz, *loc. cit.* No polarization was observed in the electrolysis of potassium iodide in fused iodine, G. N. Lewis and Wheeler, *Z. physik. Chem.*, **56**, 179 (1906). Cf. Lorenz, Elektrolyse, iii, 1 ff. for details.

are sometimes formed, and complex ions are therefore probably present. Surface tension measurements indicate strong association [1] of fused salts.

The migration of ions has been observed in fused salts,[2] but transport ratios cannot be calculated, since "solvent" is identical with "solute." In the case of a particular mixture of lead chloride and potassium chloride containing about 7 per cent of the former, all the lead deposited is taken from the vicinity of the kathode and no lead ions move through the mass of the liquid.

Lorenz and Schultze investigated the conductivity of fused zinc chloride between 250° and 700° in a hard glass cell with silver electrodes, resembling the Arrhenius cell. Lorenz and Kalmus used platinum electrodes in a hard glass or quartz cell, two circular electrodes being separated by a capillary vessel. Aten used carbon electrodes; for good conductors a peculiar type of cell was used.[3] A general source of error is the conduction of the glass at high temperatures. Arndt used porcelain U-tubes with platinum electrodes. Arndt and Gessler [4] worked up to 1100°.

The chief sources of error in the measurements are: [5] (1) evaporation of deposited metal, increasing at higher temperatures; (2) chemical side reactions (e.g., $Ca + CaCl_2 = 2CaCl$); (3) cloud formation, when the metal does not separate in compact form but is diffused through the fused electrolyte in the form of a very fine cloud or mist; [6] (4) colloidal solution of metal in the electrolyte; (5) complex formation at the anode; (6) recombination of the deposited substances. The formation of fog may be prevented to some extent by the addition of another salt, e.g., KCl to $PbCl_2$, $BaCl_2$ to $PbCl_2$, etc., the effect being supposed to depend on changes of surface tension between the metal and fused salt.[7]

The increase in current density in the electrolysis of fused salts is limited by the appearance of the so-called *anode effect*, the formation of a layer of gas between the electrode and the fused electrolyte, which results in a large increase in the electromotive force and current may then pass across the gap in the form of arcs. At a given temperature this effect sets in at a definite current density, which decreases with rise of temperature.[8]

[1] Lorenz, *Z. physik. Chem.*, **70**, 238 (1910); Walden, *Bull. Acad. Petersb.*, 405 (1914); *Z. physik. Chem.*, **75**, 555 (1910); Walden and Swinne, *ibid.*, **79**, 700 (1912); **82**, 271 (1913); Liebmann, *Diss.*, Zurich, 1909; Hochberg, *Diss.*, Frankfort a/M., 1915; Lorenz and Hochberg, *Z. anorg. Chem.*, **94**, 301 (1916).

[2] Lorenz, *Z. physik. Chem.*, **70**, 234 ff. (1910).

[3] *Z. physik. Chem.*, **66**, 653 (1909).

[4] *Z. Elektrochem.*, **14**, 662 (1908). Cf. Goodwin and Mailey, *Phys. Rev.*, **26**, 28 (1908).

[5] Lorenz, Elektrolyse, ii, 32 f.

[6] This is shown especially in the electrolysis of lead salts in electrolytes containing alkalies; it increases with temperature. See Lorenz and Helfenstein, *Z. anorg. Chem.*, **23**, 255 (1900); Schultze, *ibid.*, **20**, 323 (1899); Grünauer, *ibid.*, **39**, 389 (1904); Lorenz, Elektrolyse, i, 136 f., ii, 40 f.

[7] Lorenz, *Z. Elektrochem.*, **13**, 582 (1907); *Nernst Festschrift*, 266 (1912); Lorenz and Appelberg, *Z. anorg. Chem.*, **36**, 36 (1903); Walden, *loc. cit.*

[8] Wartenberg, *Z. Elektrochem.*, **32**, 330, 1926; Heppenstall and Schutt, *Trans. Farad. Soc.*, **20**, 97, 1924.

The conduction of fused salts is characterized by Lorenz as of the Grotthus type (see later), as contrasted with the Hittorf type (moving ions) in the case of solutions.[1] From considerations of the ionic radius he supposes that there is an exchange between ions and molecules.[2] An approximate calculation gave the dissociation of $NaNO_3$ as 31.5 per cent at 388°. The method of calculation is as follows. The Hittorf conductivity is obtained by dividing the observed conductivity by 2, since the speed of the ions is 2 to 3 times that calculated from the atomic radii, and the limiting value is found by Einstein's formula, making use of the viscosities and radii of the ions in water and in the fused salt.[3] It is assumed that the effect of temperature on the degree of ionization may be neglected.[4] Einstein's formula gives for the velocity of motion of a particle of radius r in a medium of viscosity η the value:

$$u = K/6\pi\eta r N_0,$$

where N_0 = number of molecules per gram molecule and K is the driving force applied to the particle. If K is in dynes, u is given in cm. per sec., and is then calculable. It is assumed that the mobilities in water and in the fused salt are inversely proportional to the viscosities and radii (as indicated by the formula):

$$u_w/u_s = \eta_s r_s/\eta_w r_w,$$

and further that the radius of the ion is, at least very approximately, the same in both cases, i.e., $r_s = r_w$. The value of the limiting equivalent conductivity (see later) is then given by

$$\Lambda_\infty = (u_w + v_w)\frac{\eta_w}{\eta_s},$$

also $\Lambda = \kappa/c$, where c is the concentration of the fused salt. It will be seen that the calculation is somewhat speculative in character. The measurement of the viscosities of fused salts is described by Lorenz.[5]

The high conductivities shown by most fused salts may be realized from the figures in the table, with which the conductivity of 20 per cent HCl at room temperature, $\kappa = 0.76$, may be compared.

[1] *Z. physik. Chem.*, **79**, 63 (1912); Fleck and Wallace, *Trans. Farad. Soc.*, **16**, 346 (1920), think that, since Ohm's law is strictly obeyed by fused caustic soda, the ions are already formed and no energy is required to disrupt the molecule.

[2] *Z. physik. Chem.*, **73**, 253 (1910).

[3] *Z. physik. Chem.*, **73**, 252, 330 (1910); Lowry, *Trans. Farad. Soc.*, **23**, 508 (1927); Schulze, *Z. Elektrochem.*, **19**, 122 (1913), finds the degree of ionization of fused AgCl to be 1.17×10^{-3} to 1.35×10^{-3} at 461°, and of AgBr, 2.35×10^{-4} at 450°, in agreement with Abegg's values, based on E.M.F. measurements (*ibid.*, **5**, 353 (1899)). Electrolysis of fused ICl and IBr; Bruner and Bekier, *Z. Elektrochem.*, **18**, 368 (1912).

[4] *Z. physik. Chem.*, **79**, 63 (1912); Ber., **40**, 3308 (1907); table of values of Λ_∞ in *Z. physik. Chem.*, **79**, 65 (1910).

[5] *Z. physik. Chem.*, **73**, 244 (1910): Lorenz and Appelberg, *Z. anorg. Chem.*, **36**, 36 (1903); Tubandt and Lorenz, *Z. physik. Chem.*, **87** 513 (1914); Arndt, Physikal. Chem. Technik, 1915, p. 585; Walden, *Bull. Acad. Sci. Petersb.*, 405 (1914).

TABLE I

Salt	Temperature ° C.	κ
$AgCl$	600	4.44
$NaCl$	850	3.50
KCl	850	2.28
$CaCl_2$	800	1.90
KNO_3	350	0.67
$AlBr_3$	195	c. 10^{-6}

The experiments of Poincaré (*loc. cit.*) indicate that the ionization of a fused binary salt is independent of temperature, the changes of conductivity being determined by changes of viscosity. When a fused salt solidifies, an enormous change of conductivity occurs, but Sachanow [1] considers that this is entirely accounted for by the great viscosity change, and that salts are ionized to the same extent in the solid and liquid states.

The conductivities of salts dissolved in fused salts have been measured by various investigators. The molecular conductivities of such solutions are high and usually decrease with dilution, whilst the opposite holds for aqueous solutions.[2] Measurements with chlorides of cæsium, potassium, sodium, ammonium, copper (cuprous) in fused mercuric chloride at 282° with platinum electrodes in a special apparatus were made. Solutions of mercurous chloride in the same solvent were non-conductors. Chlorides of bivalent metals are nearly all insoluble in fused mercuric chloride. Sackur [3] claimed to have found that the laws of dilute solutions held for solutions of silver and cuprous chlorides in fused sodium and potassium chlorides for concentrations up to normal. By E.M.F. measurements he found that the ionization of the solutes is of the order of 10 per cent, and is independent of concentration.

Electrolysis of solutions of lithium carbide in molten lithium hydride leads to separation of carbon at the anode, whence it is concluded [4] that the carbide is ionized. Nitrides of alkaline earth metals in the corresponding hydrides as fused solvents appear to be similarly ionized. Lithium hydride itself, in the fused state, gives hydrogen at the anode [5] and probably ionizes as $Li^+ + H^-$.

The conductivities of mixtures of fused salts [6] are less than those calculated by the mixture law, and the isotherms sometimes exhibit minima, indicating combination. No singular points are shown when combination occurs, except in the case KCl–$CaCl_2$. Benrath and Drekopf [7] measured the specific conductivity of molten mixtures of K_2SO_4 with Na_2SO_4, $MgSO_4$, KF, and Li_2SO_4. They find that the eutectic is a well-defined conductivity point. The specific

[1] *J. Russ. Phys. Chem. Soc.*, **48**, 341 (1916); Lorenz, Elektrolyse, iii, 289.

[2] Foote and Martin, *Amer. Chem. J.*, **41**, 451 (1909).

[3] *Z. physik. Chem.*, **83**, 297 (1913).

[4] Guntz and Benoit, *Compt. rend.*, **176**, 970 (1923).

[5] Moers, *Z. anorg. Chem.*, **113**, 179 (1920); Peters, *Z. anorg. Chem.*, **131**, 140 (1923); *Z. Elektrochem.*, **29**, 312 (1923); Hüttig and Krajewski, *Z. anorg. Chem.*, **141**, 133 (1925) on preparation of LiH.

[6] Sandonnini, *Atti R. Accad. Lincei*, **24**, i, 616 (1915); *Gazetta*, **50**, i, 289 (1920).

[7] *Z. physik. Chem.*, **99**, 57 (1921).

conductivity depended on temperature according to the equation which they found to hold in the case of pure fused salts.

Grotthuss' Theory of Electrolysis: An explanation of the fact that the products of electrolysis separated only at the poles was given by Grotthuss in 1805.[1] He supposed that the passage of the current and the chemical effects were due to a series of successive decompositions and recombinations of the particles of the dissolved substance. In Fig. 1*a* let *AB*, *AB*, ··· represent molecules before the current passes; these are orientated by the attraction of the poles in the manner shown. The molecule next the positive pole on the left is decomposed, the *A* atom being attracted and deposited. The *B* atom, now without a partner, takes the *A* atom from the next molecule, and this goes on until at the end of the chain the unpaired *B* atom is set free. This stage is shown in Fig. 1*b*. All the molecules rotate so as to present *A* sides to the positive pole again, as in Fig. 1*c*, and the process is repeated. The cause of decomposition is thus assumed to be the attraction of the poles, which had been assumed by Berzelius and Hisinger [2] to vary inversely as some power of the distance from the pole. This view was disproved by Faraday.[3] He connected two platinum strips, kept at a fixed distance apart, with a galvanometer and immersed them in dilute acid through which a current was flowing between two other electrodes. The deflection of the galvanometer was the same for all positions of the strips between the poles, indicating a constant force. Faraday also showed [4] that chemical decomposition could be produced without metal electrodes, e.g., by allowing the electric discharge from a pointed wire connected with a frictional machine to impinge on turmeric paper moistened with sodium sulphate solution, the other end being earthed. Alkali was liberated. He also showed [5] that when a current was passed through a strong solution of magnesium sulphate covered with a layer of water, magnesium hydroxide separated at the junction of the two liquids, although no electrode was situated there. From this and other experiments Faraday assumed that the decomposition was passed on from one salt particle to the next through the solution, and did not proceed where there were no contiguous salt particles, and he adopted a modification of Grotthuss' theory: [6] "the effect is produced by an internal corpuscular action exerted according to the direction of the electric current, due to a force either superadded to, or giving direction to the ordinary chemical affinity of the bodies present. The body under decomposition may be considered as a mass of acting particles, all those which are included in the course of the electric current

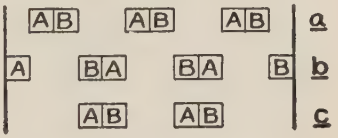

FIG. 1. Diagram illustrating Grotthuss' Theory

[1] *Ann. Chim.*, **58**, 54 (1806); **63**, 20 (1808). The first paper was printed in Rome, 1805.
[2] *Ann. Chim.*, **51**, 167 (1804).
[3] Expt. Res., 1833, 5th Series, 144.
[4] Expt. Res., 1833, 5th Series, 131.
[5] Expt. Res., 1833, 5th Series, 140.
[6] Expt. Res., 1833, 5th Series, 149.

contributing to the final effect; and it is because the ordinary chemical affinity is relieved, weakened, or partly neutralized by the influence of the electric current in one direction parallel to the course of the latter, and strengthened, or added to in the opposite direction, that the combining particles have a tendency to pass in opposite courses. . . . Particles *aa* could not be transferred or travel from the pole *N* towards the other *P* unless they found particles of the opposite kind *bb* ready to pass in the contrary direction." Also "the free substance *cannot* travel, the combined one *can*." [1] Faraday's views were far from clear. They appear to be an attempt to link up electrolytic conduction with phenomena in polarized dielectrics, two groups of phenomena which we now separate sharply.

Nomenclature: Faraday found it necessary to invent new names in the description of his experiments. The poles are only the doors or ways by which the electric current passes into or out of the decomposing body, hence they were called *electrodes* (ἤλεκτρον, amber, with which electrical effects are said first to have been observed, and ὁδὸς a way). The electrode by which the [positive] current entered was called the *anode* (ἄνω, upwards), that by which it left, the *kathode* (κατὰ, downwards). The material decomposed was called the *electrolyte* (ἤλεκτρον, and λύω, I loose). The bodies which move to the electrodes were called *ions*, that moving to the anode being the *anion* (ἀνιὼν, that which goes up, i.e., up-stream with the positive current), and that moving to the kathode the *kation* (κατιὼν, that which goes down).[2] It may be noted that, although the other terms have their modern meaning, the *ion* of Faraday had scarcely the modern significance.

Faraday distinguished between *primary and secondary products* of electrolysis.[3] The primary products are deposited as such at the electrodes, e.g., hydrogen from acids, silver from silver salts. In early experiments the metals were thought to be produced by reduction by nascent hydrogen, regarded as the primary product; this was replaced by the theory (now held) that metals were primary products by Hisinger and Berzelius,[4] their theory being accepted by Davy, but rejected by Faraday.[5] The secondary products are those formed by interaction of the primary products with the solution or electrodes. When sulphuric acid is electrolyzed, the SO_4 liberated reacts with water:

$$SO_4 + H_2O = H_2SO_4 + O.$$

The theory of the constitution of acids which represents sulphuric acid as

[1] Expt. Res., 5th Series, 157; the theory is extended by H. E. Armstrong, *Brit. Ass. Rep.*, p. 945 (1885); *Proc. Roy. Soc.*, **40**, 268 (1886) and many later papers. Armstrong considers that all chemical changes are electrolytic in character and take place under the same conditions as in a cell, viz., by the combined action of three substances (two poles and an electrolyte), one of which must be a conductor. Chemical change is thus "reversed electrolysis"; Mellor, Chemical Statics and Dynamics, 1904, p. 274.

[2] Expt. Res., 7th Series, 195; the names are due to Whewell; Daneel, Elektrochemie, i, 62 (1911).

[3] Expt. Res., 7th Series, 218.

[4] *Ann. Chim.*, **51**, 174 (1804).

[5] Expt. Res., 7th Series, 219.

$H_2.SO_4$ and not $H_2O.SO_3$ is due to Daniell,[1] who pointed out that in the electrolysis of sodium sulphate, besides soda and sulphuric acid, hydrogen and oxygen are also liberated, so that the current appears to do twice as much work in this case as it does in the electrolysis of water or hydrochloric acid, where only one set of products is formed. The hydrogen and oxygen in the first case can then be represented as secondary products, in the formation of which the current plays no part:

$$2Na + 2H_2O = 2NaOH + H_2; \qquad SO_4 + H_2O = H_2SO_4 + O.$$

LeBlanc [2] has shown, however, that in this and many other cases the hydrogen and oxygen are probably primary products, since they are more easily discharged at the electrodes than the ions Na and SO_4, which carry the current through the solution. Since the NaOH and H_2SO_4 are largely split up into ions in solution, the sodium ion, if deposited, would merely pass back into a sodium ion by reaction with water, and it is simpler to suppose that it is the H ion of the water which is directly deposited, leaving the OH ion, which along with the Na ion which has carried the current, forms *ionized* NaOH, i.e., Na and OH ions. At the other electrode 2 OH ions are deposited, forming $O+H_2O$, and the two corresponding H ions of the water give, with the SO_4 ion which has carried the current, ionized H_2SO_4, viz., $2H + SO_4$. A convincing argument in favor of this theory is that the voltage required to decompose nearly all salts in aqueous solution, with deposition of hydrogen and oxygen, is about the same, 2 volts, as it should be if the reaction is in all cases the deposition of H and OH ions of water. Thus, the old explanation that " acid is added to water to enable it to conduct the current, but it is the water which is really decomposed " happens to be right.

Faraday's Laws of Electrolysis: As a result of a long series of researches,[3] Faraday was able to summarize the quantitative results of electrolysis in two very simple laws:

1. *The amount of chemical action is proportional to the quantity of electricity which has passed through the electrolyte.*
2. *Ions are liberated by the same quantity of electricity in the proportions of their chemical equivalents.*

Thus: *the quantity of electricity which liberates one gram equivalent of an ion is always the same.* It is called the *faraday*, denoted by F, and the value is 96,500 coulombs.[4]

The weight z of ion liberated by one coulomb is called the *electrochemical equivalent;* it is the chemical equivalent divided by F:

$$z = M/yF,$$

[1] *Phil. Trans.*, **129**, 97 (1839); **130**, 209 (1840); **134**, 1 (1844). An Introduction to the Study of Chemical Philosophy, 2d edition, London, 1843, p. 534.

[2] *Z. physik. Chem.*, **8**, 299 (1891).

[3] Expt. Res., 5th Series, 145; 7th Series, 195.

[4] Washburn and Bates, *J. Am. Chem. Soc.*, **34**, 1341 (1912); Bates, *ibid.*, **34**, 1515 (1912) Bates and Vinal, *ibid.*, **36**, 916 (1914); Vinal and Bovard, *ibid.*, **38**, 496 (1916).

where M = molar, or atomic, weight; y = valence. The weight w of ion deposited by a current of I amperes flowing for t seconds is:

$$w = Izt = IMt/yF.$$

The value of F is based on the electrochemical equivalents of silver and (most recently) of iodine.[1]

An accurate value of F and a reliable method permit of accurate measurement of current by the electrochemical method.

As a result of numerous experiments Faraday's law is found to be exact, with an accuracy of 0.01 per cent in the best cases. The relation is independent of current strength (when all secondary effects are eliminated), and holds in the case of different solvents,[2] or even in the absence of solvent (fused salts).[3] The law is probably strictly exact.

The Electronic Charge: The exact proportionality between charge and mass of an ion leads almost necessarily to the assumption, made by Maxwell,[4] in 1873 that the current is carried convectively by the ions, each of which is associated with a fixed charge, the unit charge being that on a univalent ion. He says: " It is therefore extremely natural to suppose that the currents of the ions are convection currents of electricity, and, in particular, that every molecule of the cation is charged with a fixed quantity of positive electricity, which is the same for the molecules of all cations, and that every molecule of the anion is charged with an equal quantity of negative electricity " . . . " in electrolysis the motion of each ion is due to the electromotive force acting on the charged molecules. This definite quantity of electricity we shall call the molecular charge. If it were known it would be the most natural unit of electricity " . . . " one molecule of electricity." He goes on to say, however, that: " It is extremely improbable that when we come to understand the true nature of electricity we shall retain in any form the theory of molecular charges." Helmholtz [5] later put forward similar views. Faraday [6] had suggested that: " if we accept the atomic theory . . . the atoms of bodies which are equivalents to each other in their ordinary chemical action have equal quantities of electricity naturally associated with them," but he straightway throws doubt on this hypothesis. Erman [7] and R. Kohlrausch [8] suggested that ions are charged electrically. Hittorf [9] pointed out that salts, the constituents

[1] For literature see previous chapter.

[2] Kahlenberg, *J. Phys. Chem.*, **4**, 349 (1900); Speranski and Goldberg, *J. Russ. Phys. Chem. Soc.*, **32**, 797 (1900).

[3] Lorenz, *Z. anorg. Chem.*, **23**, 97 (1900); Helfenstein, *ibid.*, **23**, 255 (1900); Auerbach, *ibid.*, **28**, 1 (1901); Lorenz, Elektrolyse geschm. Salze, ii, 91 ff.; Richards and Stull, *Proc. Am. Acad.*, **38**, 409 (1902); *Z. physik. Chem.*, **42**, 621 (1903), fused $AgNO_3$ with KNO_3 and $NaNO_3$ to 1 part in 20,000. Pressures up to 1500 atm. do not affect the value of F; Cohen, *Z. Elektrochem.*, **19**, 132 (1913).

[4] *Ann. Physik*, **11**, 737 (1880).

[5] Treatise on Electricity, 1873, Art. 255–261.

[6] Expt. Res., 1834, 7th Series, 256.

[7] *Gilbert's Ann.*, **8**, 197 (1801).

[8] *Ann. Physik*, **97**, 397 (1856).

[9] See under "Migration of Ions."

of which were regarded as having the most powerful affinities, are just those substances which conduct best in solution (e.g., KCl), whilst those exhibiting weaker affinities (e.g., $HgCl_2$) are much less conducting.

On Maxwell's theory, the fundamental ionic charge, ϵ, must be equal to F/N_0, where N_0 is the number of molecules per mol. G. J. Stoney [1] in 1874 named this unit charge the *electron*, and made a rough estimate of its magnitude from the value of N_0 given by the kinetic theory of gases, thus finding 3×10^{-11} electrostatic units, which is of the right order of magnitude. Recent progress has enabled the determination of N_0 to be made with an accuracy of about 0.1 per cent, as explained in another part of this book, so that the value of the electronic charge can be determined with similar accuracy. In practice it is better to invert the calculation, starting with the value of the electronic charge determined by Millikan,[2] viz., $4.774\ (\pm 0.005) \times 10^{-10}$ electrostatic units $= 3.33442 \times 10^{-10} \times 4.774 \times 10^{-10} = 15.9188 \times 10^{-20}$ coulombs. Then: $N_0 = 96{,}500/15.9188 \times 10^{-20} = 6.06 \times 10^{23}$, which is probably the most exact value of the Avogadro constant known.

The electronic charge is capable of independent existence; it always has a negative charge, so that a negative ion is one having an excess, and a positive ion one having a defect, of electrons, as compared with the neutral atom. A positive electron in the same sense does not exist, since although the mass of the negative electron is only 1/1848 that of the lightest atom (hydrogen), the smallest positive charge known, equal but opposite in sign to the negative electron, is the hydrogen ion, or, according to the prevalent theory of atomic structure, the positive nucleus of the hydrogen atom, produced from the latter by removal of the orbital electron. This fundamental positive charge is now called the *proton*.[3]

In metallic conduction, the metal is assumed to consist of free electrons and positive ions of metal, and the electrons only move, in the opposite direction to the conventional current. In electrolytes, both positive and negative charges move in association with ions, but the current is not usually carried equally by both ions.[4]

Theory of Electrolytic Dissociation: It is but a step from the considerations advanced to the assumption that ions move in a state of freedom, but the actual order of discovery reversed this procedure, and the electrolytic ions were postulated before it was possible to demonstrate the existence of free electrons. Grove,[5] from experiments on the gas battery, assumed that in

[1] *Proc. Dublin Soc.*, **3**, 51 (1881); *Phil. Mag.*, **11**, 384 (1881); the original communication was made to the British Association meeting in 1874.

[2] The Electron, 1917; *Phys. Rev.*, **2**, 109 (1913); *Phil. Mag.*, **34**, 1 (1917); *Z. physik. Chem.*, **116**, 65 (1925)—Nobel lecture; Perrin, Les Atomes, 1921 (Eng. tr. 1923), Chaps. III and IV.

[3] According to Aston, Isotopes, p. 92, the name was suggested by Rutherford at the British Association Meeting in 1920.

[4] See "Migration of Ions." In some cases practically all the current is carried by one ion, and in solutions of alkali metals in non-aqueous solvents, it may be carried by free electrons.

[5] *Phil. Mag.*, **27**, 348 (1845).

the separation of hydrogen and oxygen from water no decomposition of the water molecule occurred. Williamson [1] assumed an exchange of radicals in solutions of mixed salts; he made the assumption that, in a solution of hydrochloric acid, exchange occurs between H and Cl atoms in different molecules. It would perhaps be reading too much into his speculations to assume that they foreshadowed the theory of electrolytic dissociation. Clausius [2] adopted Williamson's theory of interchange of radicals, on kinetic grounds, but he, also, assumed it to take place to a very small extent only. This agreed, as he pointed out, with the fact that a very small E.M.F. only is required to electrolyze silver nitrate between silver electrodes, so that practically no work was used up in splitting up molecules.

Arrhenius [3] first assumed that salts in solution are *extensively* broken up into ions, i.e., *electrolytically dissociated*, or *ionized*. In very dilute solutions the ionization, which increases with the dilution, becomes in many cases practically complete. This theory explained the abnormally large osmotic pressures of solutions of electrolytes, and a similar explanation was put forward independently by Planck [4] from another point of view. In both cases it was recognized that, if the laws of dilute solution are to remain valid, an increase in the number of particles must have occurred in the solution of an electrolyte.

This theory, naturally, met with little support from the conservative chemist, but although many attempts to bring forward really destructive objections have been made, the development of physics has put the theory on a very solid foundation. In its most modern form, in fact, the theory assumes even the solid salt to be made up of ions, and some go so far as to assume complete ionization of salts both in the solid and dissolved forms. The examination of crystals by X-rays has indicated that sodium chloride, for example, consists not of NaCl molecules but of Na^+ and Cl^- ions arranged in a space lattice, and in solution such a crystal would simply fall apart into its ions.[5] Such a constitution of salt crystals is in agreement with their optical and elastic properties, and with the theories of atomic structure.

The notation used in representing ions, due to Ostwald,[6] is to write the symbol of the ion, with a number of dots or dashes for the number of units of positive or negative charge, respectively, carried by the ion. This number represents at the same time the valence of the ion. Thus:

$$H_2SO_4 \rightleftharpoons H^{\cdot} + HSO_4' \rightleftharpoons H^{\cdot} + H^{\cdot} + SO_4''$$

represents the progressive ionization of sulphuric acid on the assumption that ionization increases with dilution and that ions and molecules are in chemical equilibrium. Ionization may occur in stages, and except at high dilution,

[1] *Ann. Chem.*, **77**, 37 (1851); *J. Chem. Soc.*, **4**, 110 (1852).

[2] *Ann. Physik*, **101**, 338 (1857).

[3] *Z. physik. Chem.*, **1**, 831 (1887); Harper's *Science Series*, vol. 4, p. 47.

[4] *Ann. Physik*, **32**, 462 (1887); *Z. physik. Chem.*, **1**, 577 (1887).

[5] Cf. B. Cabrera, *Anal. Fis. Quim.*, **16**, 186 (1918).

[6] Grundriss der Allgemeinen Chemie, Leipzig, 1909, p. 441; cf. Walker, *Chem. News*, **84**, 162 (1901).

usually the first stage only is appreciable. According to Harkins and Pearce [*J. Am. Chem. Soc.*, 38, 2679, 1916] all electrolytes which form more than two ions undergo stepwise dissociation and yield intermediate ions, but the usual view is that in many cases of salts the ionization occurs directly: $K_2SO_4 = 2K + SO_4''$, and that intermediate ions, such as KSO_4', if present at all, occur only in minute amounts. Harkins and Pearce, however, assume large concentrations of such ions, e.g., in 0.1 *n* solution the percentages are $K_2SO_4 = 5$; $KSO_4' = 35.2$; $SO_4'' = 59.8$. (See p. 674.) The sum of the positive and negative charges on the ions is always zero, since the solution is electrically neutral. The charged ions in electrolysis are attracted to the electrodes of opposite sign, and give up their charges. The uncharged particles may be capable of independent existence, or may form molecules of the same composition, or may react with the solvent to form secondary products.

Whether ionization is due simply to the falling apart of the two parts of a molecule on solution, or whether it is due to the previous interaction between solute and solvent,[1] cannot be said to have been definitely decided. Kendall[2] adopts the second supposition, and concludes that two non-associated substances which are chemically inert do not give a conducting solution. Ionization is always accompanied by interaction between solute and solvent. Tendency to compound formation (solvation) and ionization are parallel, and ionization in general is supposed to be preceded by compound formation. This union of the so-called "chemical" theory of solution and the theory of electrolytic dissociation is interesting and promising, but it does not yet rest on sufficient evidence on the non-aqueous side.

Evidence for the Theory of Electrolytic Dissociation: The theory of Arrhenius has a good deal of experimental evidence which may be called upon in its support.[3] This may be summarized as follows:

1. The qualitative reactions of such substances as KCl and $KClO_3$ indicate that the reactions of chlorides are due to the chloride ion and not merely to chlorine present in the molecule. $KClO_3$ gives the ions $K^{\cdot}$ and ClO_3'. In quantitative analysis, also, the effects of excess of reagent are explained by the theory (see "Solubility Product").

2. The additive properties of solutions are clearly explained by the theory. Valson showed that the surface tensions[4] and densities[5] of salt solutions could be regarded as the sum of three separate magnitudes, characteristic of the solvent, the metallic constituent (kation), and the acid radical (anion). Other

[1] Ciamician, *Z. physik. Chem.*, **69**, 96 (1909).

[2] *Proc. Nat. Acad. Sci.*, **7**, 56 (1921); Kendall and Booge, *J. Am. Chem. Soc.*, **39**, 2323 (1917); Kendall and Gross, *ibid.*, **43**, 1416, 1426 (1921); Kendall, Davidson and Adler, *ibid.*, **43**, 1481 (1921); Kendall and Andrews, *ibid.*, **43**, 1545 (1921); Partington, *J. Chem. Soc.*, **97**, 1158 (1910).

[3] Arrhenius, Faraday Lecture, *J. Chem. Soc.*, **105**, 1414 (1914); Gibbs Address, *J. Am. Chem. Soc.*, **34**, 353 (1912); *Trans. Farad. Soc.*, **15**, 10 (1919); cf. Dhar, *Z. Elektrochem.*, **22**, 245 (1916); for difficulties in Arrhenius' theory see Ebert, *Jahrb. d. Radioakt.*, **18**, 134 (1921).

[4] *Ann. Chim. Phys.*, **20**, 361 (1870).

[5] *Compt. rend.*, **73**, 441 (1874).

additive properties were shown to follow the same rule, indicating the separate existence of ions in the solution,[1] notably the heat of neutralization of a strong acid by a strong base in dilute aqueous solutions. This is always 13.65 kgm. cal., the heat of formation of water from ions: $H^{\cdot} + OH' = H_2O$, e.g., $H^{\cdot} + Cl' + Na^{\cdot} + Cl' = Na^{\cdot} + Cl' + H_2O$ + 13.65 kgm. cal. This result has been confirmed *exactly* by the refined experiments of T. W. Richards and Rowe,[2] who find that the heats of neutralization of potassium, sodium and lithium hydroxides by hydrochloric, hydrobromic, hydriodic and nitric acids at 20°, when extrapolated *through a short range* to infinite dilution, vary only between the limits 13.62 and 13.69 kgm. cal.

3. The calculation of the diffusion coefficient of a salt from the conductivity, and the effect of chlorides on the diffusion of hydrochloric acid,[3] are in perfect agreement with the theory.

4. The colors of solutions at high dilution should be additively composed of those of the solvent and the two ions. With an uncolored solvent, such as water, and one ion uncolored, all solutions of salts with a common colored ion, e.g., all permanganates, should show the same absorption spectrum. This was confirmed by Ostwald.[4]

5. The experimental fact that the equivalent conductance, Λ, increases with dilution, but ultimately approaches a limiting constant value at high dilution, is very simply explained by the theory.

6. The excellent agreement of Ostwald's dilution law (*q.v.*) for weak acids and bases is strong evidence for the theory. The disagreement with strong electrolytes is a difficult problem, but no suggestion towards an explanation of the deviation has been made which does not assume electrolytic dissociation in some form or other. At very high dilutions the law may hold even for strong electrolytes.[5]

7. The abnormal freezing point depressions for aqueous solutions of salts are explained by the theory. Noyes and Falk [6] show that for solutions not more concentrated than 0.1 *n.* the ionization calculated from the freezing point does not differ from that calculated from conductivity by more than 2 per cent in the case of electrolytes containing two univalent ions. Hygroscopic salts with bivalent kations show greater depressions than calculation requires. In a valuable series of papers Noyes and Falk have collected the

[1] Ostwald, Lehrbuch, vol. 1, "*Salzlösungen.*"

[2] *J. Am. Chem. Soc.*, **44**, 684 (1922); cf. Hess, *Ann. Physik*, **50**, 385; **52**, 97 (1842).

[3] Arrhenius, *Z. physik. Chem.*, **10**, 74 (1892).

[4] *Z. physik. Chem.*, 9, 579 (1892); cf. however papers by Houstoun, Anderson, Brown, Cochrane and Gray in *Proc. Roy. Soc. Edin.*, 1910–1913. Wright, *J. Chem. Soc.*, **103**, 528, (1913); **105**, 669 (1914), finds that strong acids exert the same absorptive power on light as their salts, whilst weak acids (little dissociated) often show great variations, as would be expected. See also the interesting papers of Schäfer, *Z. anorg. Chem.*, **97**, 285; **98**, 70 (1919); *Z. physik. Chem.*, **93**, 312 (1919); and Hantzsch, *Ber.*, **50**, 1422 (1917) and many later papers.

[5] Washburn and Weiland, *J. Am. Chem. Soc.*, **40**, 131, 151 (1918); Nernst, *Z. Elektrochem.*, **33**, 428 (1917)—see p. 659.

[6] *J. Am. Chem. Soc.*, **34**, 454 (1912).

data for freezing point lowering,[1] transport numbers,[2] and conductivity[3] of aqueous solutions. In the last paper the values of the ionization of the salts at various dilutions are given. The ionization is not an additive property with respect to the ion constituents, and is not related to the mobilities of the ions. The ionizations at 18° and 25° agree within the limits of experimental error.

8. The velocity of reaction shows that those acids are strongest which are most conducting in solution, and Ostwald thought that the catalytic activity of acids in hydrolyzing methyl acetate was proportional to the conductivity. Arrhenius in 1889 showed that the activity was proportional to the $H^{\cdot}$ ion concentration, but recent work has modified this view.

Specific, Equivalent, and Molar Conductance: The relation between resistance, current, and pressure (potential difference between the ends of a conductor) was summarized by G. S. Ohm[4] in the well-known law. If R is the resistance, E the electric pressure, and I the current, then $E = kIR$, where k is a factor depending only on the choice of units and can be made equal to unity. The *International Ohm* is the unit of resistance and is defined as the resistance offered to an unvarying current by a column of mercury at the temperature of melting ice, 14.4521 grams in mass, 106.300 cm. in length, and of constant cross section. The *International Ampère* is the unit of current and is defined as the unvarying electric current which when passed through a solution of silver nitrate in water, in accordance with specified conditions, deposits silver at the rate of 0.00111800 gram per second. The *International Volt*, the unit of electric pressure, is then defined by Ohm's law as the electric pressure which, when steadily applied to a conductor the resistance of which is one International Ohm, will produce a current of one International Ampère.

If a conductor of length L cm. and uniform cross section A sq. cm. has a resistance R, then $r = RA/L$ is called the *specific resistance*, or *resistivity*, of the material of the conductor. The *conductance* is the reciprocal of the resistance, and the *specific conductance*, or *conductivity*, of the material is

$$\kappa = 1/r = L/RA.$$

Thus

$$R = Lr/A = L/\kappa A.$$

If a liquid is contained in an electrolytic cell, and if $\kappa = C/R$, where R is the resistance of the cell, then C is called the *cell constant*. It may be determined with a liquid of known conductivity in the cell.[5]

[1] *J. Am. Chem. Soc.*, **32**, 1011 (1910).

[2] *Ibid.*, **34**, 454 (1912).

[3] *Ibid.*, **33**, 1436 (1911).

[4] Die galvanische Kette, mathematisch bearbeitet, Berlin, 1827; he does not use the term "resistance," but speaks of "reduced lengths" of conductors.

[5] The cell constant applies only to a particular temperature; Washburn, *J. Am. Chem. Soc.*, **38**, 2431 (1916). Schlesinger and Read, *ibid.*, **41**, 1727 (1919), state that C should be determined with solutions covering the whole range of conductances to be measured with the cell.

If the cell is a cylinder of length L and section A, and if the electrodes fill the section completely, then[1] $C = L/A$.

As standard liquids Kohlrausch[2] recommends a number of solutions, but in many cases these are suitable only for approximate work. The standard is normal potassium chloride solution made up from 74.555 grams of pure KCl weighed in air and diluted to 1 litre at 18°. This should have a density of 1.04492 at 18°.[3] $\kappa = 0.09822$ at 18°.

Other solutions of KCl prepared by dilution of the normal are $n/10$, $n/50$ and $n/100$, with conductivities of 0.01119, 0.002397 and 0.001225, respectively, according to Kohlrausch.

Parker and Parker[4] point out that, with the ordinary definition of cell constant, the concentrations of the solutions should be expressed in equivalents per *cubic decimetre*, not per litre (1 litre = 1.000027 cu. deci.), and unit concentration is then *demal* (D) not *molal* or *normal* (which refer to a litre). They also find that the value of the " cell constant " depends on the voltage and frequency of the current, and on the electrolyte. They suggest the following solutions for standardizing cells, the weights in grams in air of KCl being added to 1000 grams of water also weighed in air. Tables of values for temperatures from 0° to 30° are given and a comparison with older data. The values of κ on the new basis are lower, *e.g.*, by about 0.145 per cent as compared with Kohlrausch

TABLE II

Concentration	Grams KCl to 1000 gm. H_2O	Conductivity in ohm. cm.$^{-1}$		
		0°	18°	25°
1 D	76.6276	0.065098	0.097790	0.111322
0.1 D	7.47896	0.0071295	0.0111636	0.0128524
0.01 D	0.746253	0.00077284	0.00122023	0.00140789

and Maltby's figures. The last place of decimals is uncertain. The variability in the cell constant has led to the expression of the opinion[5] that " relatively large errors of an indeterminate amount exist in published conductance data." The good agreement between the results of Kohlrausch and Maltby and those of Washburn makes this very improbable if the usual meaning of

[1] Kohlrausch and Holborn, Leitvermögen der Elektrolyte, 1916, p. 12.

[2] Leitvermögen, p. 76 ff.; G. Eastman, *J. Am. Chem. Soc.*, **42**, 1655 (1920).

[3] Washburn, *loc. cit.*, determines cell constants with a solution of 7.43000 grams KCl in 1000 grams of *solution* (weights in air); κ at 25° = 0.01288; at 0° κ = 0.00715. Kraus and Parker, *J. Am. Chem. Soc.*, **44**, 2422 (1922), propose to take 0.1 KCl with $\kappa = 0.011203$ at 18° from Kohlrausch and Maltby's results, and find then κ at 25° = 0.0128988. Graetz in Winkelmann's Physik, IV, i, 331, gives weights *in vacuo*.

[4] *J. Am. Chem. Soc.*, **46**, 312 (1924).

[5] Randall and Vanselow, *J. Am. Chem. Soc.*, **46**, 2418 (1924); Randall and Scott, *ibid.*, **49**, 637 (1927).

"large errors" is intended. Redlich [1] describes a method of compensation using uncharged electrodes in which the effect of varying cell capacity can be eliminated.

Equivalent Conductance: The conductivity of a solution depends on its concentration. The *equivalent conductance*, Λ, is defined as the conductivity divided by the concentration, η, in equivalents *per cc.* (not per litre), $\Lambda = \kappa/\eta$, where the reciprocal of concentration, $\varphi = 1/\eta$, is called the *dilution*. The name equivalent conductance is due to Lenz.[2]

If a volume of solution containing one equivalent of solute is poured into a cell formed of parallel plates one centimeter apart, the conductance will be equal to the equivalent conductance. For, the liquid may be divided into φ cubical cells each of unit volume, and each will have the specific conductance κ. Thus the total conductance will be: $\kappa\varphi = \kappa/\eta = \Lambda$.

The *molar conductance*, μ, used by Ostwald, is defined as the conductivity divided by the concentration c in mols per litre $\mu = \kappa/c$. In making use of the values of μ given by Ostwald and by H. C. Jones and his co-workers it is necessary to remember that they are based on the Siemens resistance unit, and require multiplication by 1.066 to reduce to reciprocal ohms. They have been recalculated by Kohlrausch.[3]

If concentrations are in mols and equivalents per c.c. or per litre in both cases, then $\mu = \nu\Lambda$, where ν is the sum of the valencies of the anions or cations (e.g., $\nu = 2$ for H_2SO_4, $CaCl_2$, $MgSO_4$, etc.). [Lorenz, *Z. anorg. Chem.*, 106, 50 (1919).]

For good conductors the influence of the conductivity of the solvent itself may be neglected, but at high dilutions it is usual to subtract the conductivity of the solvent, κ_0, from the total conductivity, and [4] to define Λ as $(\kappa - \kappa_0)/\eta$. Ostwald [5] in 1885 pointed out that this leads to impossible values in the case of acids and bases in dilute solutions, and suggested that this was due to chemical interaction between the solute and impurities in the water. This makes the determination of equivalent conductances of acids and bases in very dilute solutions a matter of very considerable difficulty.

The values of Λ so far determined, with the exception of very recent ones, are collected in Kohlrausch and Holborn's Leitvermögen der Elektrolyte. More recent determinations are given in Landolt-Börnstein's *Tabellen* and in the International Critical Tables; a useful summary is Scudder's Electrical Conductivity and Ionization Constants of Organic Compounds, London, 1914; the collected monographs of H. C. Jones and co-workers and of Noyes will be

[1] *Z. physik. Chem.*, **136**, 331 (1928).

[2] *Ann. Physik*, **160**, 425 (1877).

[3] Leitvermögen; see also Whetham, Theory of Solution, 1902, 407 ff.; it must also be remembered that different values of the ohm, atomic weights, and concentration units, all affect the results. On correction for atomic weights see Kohlrausch, *Z. physik. Chem.*, **72**, 43 (1910).

[4] Arrhenius, *Bih. Svensk. Akad. Handl.*, **8**, Nr. 13 (1884); Kohlrausch, *Ann. Physik*, **26**, 161 (1885). This procedure will be discussed later.

[5] *J. prakt. Chem.*, **140**, 300 (1885).

found in the Carnegie Institute Reports. Work at high temperatures was carried out by Noyes and co-workers.[1]

The following table gives a selection of equivalent conductances at 18°, concentrations being in equivalents per *litre*.

TABLE III

Conc. eq./lit.	0.0001	0.001	0.01	0.1	1	10
KCl	129.1	127.3	122.4	112.0	98.3	——
NaCl	108.1	106.5	102.0	92.0	74.3	——
KNO_3	125.5	123.6	118.2	104.8	80.5	——
$AgNO_3$	115.0	113.2	107.8	94.3	67.8	——
$\frac{1}{2}CaCl_2$	115.2	112.0	103.4	88.2	67.5	——
$\frac{1}{2}Pb(NO_3)_2$	120.7	116.1	103.5	77.3	42.0	——
$\frac{1}{2}ZnSO_4$	110	98.8	73.2	45.6	26.6	——
$\frac{1}{2}CuSO_4$	110	98.5	71.7	43.9	25.8	——
HCl	——	377	370	351	301	64.4
HNO_3	——	375	368	350	310	65.4
$\frac{1}{2}H_2SO_4$	——	361	308	225	198	70
NaOH	——	208	200	183	160	20.2
KOH	——	234	228	213	184	44.8
CH_3COOH	107	41	14.3	4.6	1.32	0.049

Experimental Determination of Electrolytic Conductivity: Many attempts were made to determine conductances of solutions before a satisfactory method was found. Apart from errors due to insufficient attention to the effect of temperature, the chief error in older work was that caused by polarization of the electrodes. When finite deposition of ions on the electrodes occurs, a cell is set up, the electromotive force of which opposes that driving current through the solution. Unless a pressure in excess of the force of polarization is applied to the terminals of the cell no current flows, whilst according to Ohm's law the smallest applied pressure should lead to the corresponding current. As a final result of experiments it was shown that, provided polarization was eliminated, Ohm's law is accurately followed, and electric pressure and current vanish together.

Direct current measurements were made by Horsford,[2] who passed a current between two electrodes in a rectangular trough, and then moved them closer together. The current increased, but by inserting a wire in series it could be restored to its original value. Horsford assumed that the effect of polarization was the same in both positions of the plates, and the resistance of the wire then gave that of a column of liquid equal in length to the distance through which the plates were moved nearer together. The method was

[1] *Z. physik. Chem.*, **70**, 335 (1910); see also references in the first edition of this book, pp. 513–4.

[2] *Ann. Physik*, **70**, 238 (1847); Malmström, *Z. physik. Chem.*, **22**, 331 (1897); Christiansen, *Chem. Soc. Abstr.*, ii, 9 (1921); Morgan and Hildburgh, *J. Am. Chem. Soc.*, **22**, 304 (1900).

improved [1] by using electrodes of the metal present in solution, when polarization was reduced.[2] Further improvements were made by Beetz [3] who used amalgamated zinc plates in zinc sulphate solution, when polarization was almost eliminated. In the method due to Fuchs [4] a constant current is passed through a solution and the drop in potential between two points measured by secondary electrodes connected with an electrometer. Bouty used zinc rods in solutions of zinc sulphate as subsidiary electrodes; recent experimenters use calomel (Newberry) or hydrogen (Marie and Noyes) electrodes. The method is capable of some accuracy.

Stroud and Henderson [5] used two narrow tubes of equal diameter but unequal lengths as two arms of a Wheatstone's bridge, the other two being composed of equal coils. Resistance was added to the shorter tube till the bridge was balanced. The assumption is made that the effects of migration and polarization are equal in the two tubes, and the added resistance is then equal to the resistance of the liquid column equal in length to the difference between the two tubes.

Beetz [6] eliminated electrodes altogether by making use of currents induced in the liquid by a moving magnet.

The most satisfactory method of eliminating polarization is the use of alternating currents of sufficiently high frequency,[7] combined with platinum electrodes coated with platinum black,[8] which expose a large surface and so reduce as far as possible the surface density of the ions deposited, to which the E.M.F. of polarization is proportional. The platinum is deposited on the electrodes from a solution of 1 gram of chloroplatinic acid and 0.008 gram of lead acetate in 30 cc. of water. The electrodes are immersed in this and current from two accumulators passed backwards and forwards between the electrodes, with reversals every few minutes. A resistance is inserted so

[1] G. Wiedemann, *Ann. Physik*, **99**, 177 (1856).

[2] Cf. W. Schmidt, *Ann. Physik*, **107**, 539 (1859); R. Lenz, *Bull. Acad. Petersb.*, **22**, 439 (1876); *Ann. Physik*, **160**, 425 (1877).

[3] *Ann. Physik*, **117**, 1 (1862); Waltenhofen, *ibid.*, **134**, 218 (1868); Tollinger, *ibid.*, **1**, 510 (1877); Paalzow, *ibid.*, **136**, 489 (1869); Berggren, *ibid.*, **1**, 499 (1877); Freund, *ibid.*, **7**, 44 (1879).

[4] Fuchs, *Ann. Physik*, **156**, 156 (1875); Bouty, *J. de Phys.*, **3**, 325 (1884); **6**, 5 (1887); *Ann. Chim. Phys.*, **14**, 36, 74 (1888); Sheldon, *Ann. Physik*, **34**, 122 (1888); Rasehorn, *Diss.*, Halle (1889); Newberry, *J. Chem. Soc.*, **113**, 701 (1918); Eastman, *J. Am. Chem. Soc.*, **42**, 1648 (1920); Marie and W. A. Noyes Jun., *J. Am. Chem. Soc.*, **43**, 1095 (1921).

[5] *Phil. Mag.*, **43**, 19 (1897); *Proc. Phys. Soc. London*, **15**, 13 (1897); Watson, Practical Physics, London (1908), p. 481.

[6] *Ann. Physik*, **117**, 1 (1862); Guthrie and Boys, *Phil. Mag.*, **10**, 328 (1880).

[7] F. W. Kohlrausch and Nippoldt, *Götting. Nachr.*, 415 (1868); 1 (1869); *Ann. Physik*, **138**, 280, 370 (1869); Smith and Moss, *Proc. Phys. Soc. London*, **25**, 133 (1913); Taylor and Acree, *J. Am. Chem. Soc.*, **38**, 2396, 2403, 2415 (1916); Taylor and Curtis, *Phys. Rev.*, **6**, 61 (1915).

[8] F. W. Kohlrausch and Grotrian, *Gotting. Nachr.*, 405 (1874); *Ann. Physik*, **154**, 1, 215 (1875); Lummer and Kurlbaum, *Verh. Deut. Phys. Ges.*, **14**, 56 (1895); Wien, *Ann. Physik*, **58**, 57 (1896). Roth (*Z. Elektrochem.*, **33**, 508 (1927) found that brominated pure silver electrodes give good results, especially if platinised as usual. These are attached to a short length of platinum wire for fusion through glass.

that a gentle evolution of gas occurs, and a fine deep black coating of platinum, free from lead, is deposited. The electrodes are then immersed for some hours in warm distilled water, frequently changed, to remove adsorbed salt. The removal of the last traces of platinizing liquid and occluded chlorine from the electrodes may be effected [1] by placing the electrodes in a solution of sodium acetate or dilute sulphuric acid and passing a direct current for about 15 minutes reversing the current every minute. They are then washed. If the electrodes are allowed to dry, they are afterwards wetted with difficulty: they may then be washed with absolute alcohol and then with water, but are best kept standing in water. In the case of alcoholic solutions, and solutions of silver salts and of cobaltammine salts [2] oxidation or other complicating changes may occur, and unplatinized platinum is then used. Whetham [3] reduces adsorption of salts from dilute solutions by heating the platinized electrode to redness, when a grey surface is obtained, non-adsorbent, and sufficient to prevent polarization. In accurate work with a series of solutions, it has been found better to make the measurements with the concentrated solutions first, since the amount of salt adsorbed by the electrodes does not seem to vary much with the concentration of the solution. Hence, if salt is adsorbed from the concentrated solutions (in which case the effect of the withdrawal of very small amounts of salt is inappreciable) it does not come off again into the dilute solutions and there is no tendency for salt to be taken from the latter, which would cause appreciable error. If the dilute solutions are used first, a considerable proportion of the dissolved salt is withdrawn and the conductance as measured is too low (Randall and Scott, *J. Am. Chem. Soc.*, 49, 636, 1927; A. R. Martin, *J. Chem. Soc.*, 1928, 3275). The electrodes after a time require replatinizing. The preparation of the platinum foil for the electrodes, which should be free from iron and calcium, is described by Kohlrausch.[4]

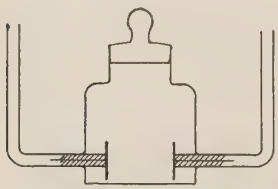

Fig. 2. Conductivity Cell

Conductivity Cells: Numerous types of conductivity cell have been described,[5] but for ordinary measurements the writer finds the cell shown in Fig. 2 satisfactory. It can be made in different sizes, with the space between the electrodes suited to the electrolyte. Cells with sliding electrodes, or electrodes easily distorted, should be avoided. The electrodes are of stout sheet platinum, with platinum wires welded on and covered

[1] Findlay, Practical Physical Chemistry, 4th ed., p. 153, 1923.

[2] Partington, *J. Chem. Soc.*, **99**, 1937 (1911); Lorenz and Posen, *Z. anorg. Chem.*, **96**, 81 (1916); Nernst and Löb, *Z. physik. Chem.*, **2**, 948 (1888); see also Haworth, *Trans. Farad. Soc.*, **16**, 365 (1920).

[3] *Phil. Trans.*, **194**, 321 (1900); Kellner, *Ann. Physik*, **57**, 79 (1896).

[4] Leitvermögen, p. 11; platinized glass electrodes, see Meillère, *J. Pharm. Chim.*, **21**, 311 (1920); effect of platinizing, see Taylor and Acree, *J. Am. Chem. Soc.*, **38**, 2415 (1916); the effect of frequency on the apparent resistance decreases as the area of surface exposed increases. There is a specific relation between the electrolyte, the electrode material and surface, and the change of capacity and resistance with frequency of the alternating current.

[5] Kohlrausch, Leitvermögen, p. 12 ff.; Rice, *J. Ind. Eng. Chem.*, **12**, 1202 (1920); Miles, *Proc. Roy. Soc. Edinb.*, **35**, 138 (1915); Acree and Robertson, *J. Phys. Chem.*, **19**, 381 (1915);

with glass inside the cell. The side tubes contain a few drops of mercury to make contact with copper wires, prolonged by rubber tubing so that the cell may be placed in the thermostat. The cell is filled almost to the stopper, which is then firmly fitted and covered with a little Faraday cement.

Fig. 3. Dipping Electrode Cell

Dipping electrodes, Fig. 3, are often convenient. The platinum wires and electrodes must be stout, so that they are not displaced by the liquid. All cells should be of good glass; Jena 16 III is not attacked by water and seals directly into platinum. For special work metal cells have been used.[1] The design of conductivity cells has been considered in detail by Washburn.[2] The area of cross section must not be less than a fixed value determined by: (i) the audibility current in the telephone used as indicator, (ii) the conductivity of the liquid having the maximum desired resistance in the cell, (iii) the density of the liquid, (iv) the heat capacity and temperature coefficient of resistance of this liquid, and (v) the percentage accuracy demanded in the measurement. It does not depend on the distance between the electrodes. When the heating effect of the current is brought into consideration, the resistance of the slide wire and telephone and the time required to make a bridge setting also come in. Washburn has devised certain types and sizes of cell, adapted to measurements with (*a*) water or very dilute solutions, (*b*) dilute solutions, (*c*) concentrated solutions. As finally set up,[3] these are shown in Fig. 4. Those of type (*a*)

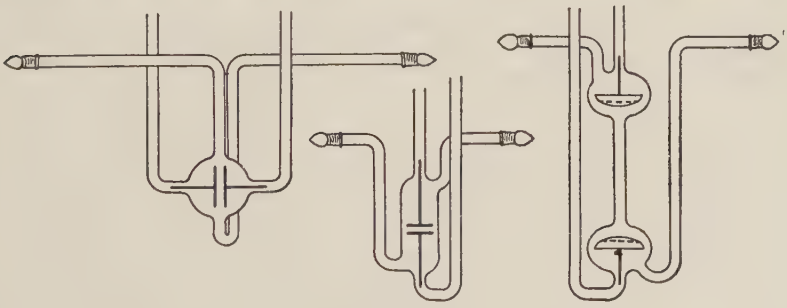

Fig. 4*a* Fig. 4*b* Fig. 4*c*

Figs. 4*abc*. Conductivity Cells—Washburn Types

Robbins, *J. Am. Chem. Soc.*, **39**, 646 (1917); theory of design of cells, Washburn, *J. Am. Chem. Soc.*, **38**, 2431 (1916); Leeds and Northrup Catalog No. 48 (1919); other cells, J. and G. E. Gibson, *Proc. Roy. Soc. Edinb.*, **30**, 254 (1910); Hill and Sirkar, *Proc. Phys. Soc. London*, **83**, 130 (1909) (wax cell for HF); Randall and Scalione, *J. Am. Chem. Soc.*, **48**, 1486 (1926).

[1] McBain and Taylor, *Z. physik. Chem.*, **76**, 179 (1911) (silver); Bowden, *J. Chem. Soc.*, **99**, 192 (1911) (silver); Noyes and Coolidge, *Z. physik. Chem.*, **46**, 323 (1903) (platinum); Kato, *Mem. Coll. Sci. Eng. Kyoto*, **i**, 332 (1908) (platinum).

[2] *J. Am. Chem. Soc.*, **38**, 2436 (1916).

[3] Leeds and Northrup Catalog No. 48 (1919), p. 25 f.

have electrodes which are unplatinized, those of type (*b*) have lightly platinized, and those of type (*c*) heavily platinized, electrodes. The bridge leads are connected with the cell leads by a pair of mercury cups dipping into the bath containing the cell, to prevent flow of heat between the cell plates and the room. The cells are of the pipette type, the ends of the inlet tubes being covered with ground glass caps.

Jena glass is sufficiently resistant for all solutions made up and [1] handled in air; in such cells conductivity water with a specific conductance of 0.21 $\times 10^{-6}$ ohm^{-1} can be kept 12 hours without change, and even after several weeks does not rise above 0.6×10^{-6} ohm^{-1}, the contamination in this case certainly coming from the atmosphere.[2] The use of quartz cells is necessary in work of very high accuracy. The cells should be carefully annealed and aged before use. Large changes of temperature lead to thermal strains which alter the distance between the electrodes.

The Alternating Current: The alternating current is normally supplied by a small induction coil, having a high frequency hammer. Such coils are specially supplied. Kohlrausch [3] gives the dimensions of the core as 8 cm. long and 1 cm. thick, of solid soft iron, on which are wound 200 turns of 0.5 mm. copper primary and 2000 turns of 0.25 mm. copper secondary. One accumulator with a resistance is sufficient. The contact hammer is the most important part; it is often necessary to replace the one supplied by a spring giving the right frequency. The contacts should be well platinized. Satisfactory results are only attained by trial and patience, but it is quite unnecessary except for the work of highest precision to use any other source of current.[4]

Stretched horizontal steel wires have been used [5] instead of hammers, and high frequency apparatus is described by Nernst.[6] These may be regarded as superseded by the valve oscillator. In the work of Washburn [7] a high frequency generator giving a pure sine wave current of single frequency was used.

[1] Kohlrausch, *Ber.*, **26**, 2998 (1893); Foerster, *ibid.*, **26**, 2915 (1893).

[2] Washburn, *J. Am. Chem. Soc.*, **38**, 2455 (1916); Kraus and Parker, *J. Am. Chem. Soc.*, **44**, 2429 (1922)—Λ_0 for HIO_3 is 0.9 per cent higher in quartz than in glass; Parker, *ibid.*, **45**, 2017 (1923)—Λ_0 for HCl at 25° is 425.69 in quartz cell.

[3] Leitvermögen, p. 26.

[4] Various types of current producers, Taylor and Acree, *J. Am. Chem. Soc.*, **38**, 2396 (1916); their judgment of the Vreeland oscillator may now be revised in the light of the results of Morgan and Lammert, *ibid.*, **48**, 1220 (1926); J. C. Ghosh, *J. Am. Chem. Soc.*, **36**, 2333 (1914); **37**, 733 (1915), finds that an alternating current superposed on direct current reduces polarization; this had previously been described by Reitlinger, *Z. Elektrochem.*, **20**, 261 (1914), and by Wartenberg and Archibald, *ibid.*, **17**, 812 (1911).

[5] Melde, *Ann. Physik*, **24**, 497 (1884); Wien, *ibid.*, **42**, 593 (1891); **44**, 681 (1891); Nernst, *Z. physik. Chem.*, **14**, 622 (1894); Rubens, *Ann. Physik*, **56**, 27 (1895); Orlich, *Elektrotechn. Z.*, **26**, 502 (1903).

[6] *Ann. Physik*, **60**, 600 (1897); Cohn, *ibid.*, **21**, 646 (1884); Erskine, *ibid.*, **62**, 454 (1897); Nernst and Lerch, *ibid.*, **15**, 836 (1904).

[7] *J. Am. Chem. Soc.*, **38**, 2431 (1916).

The Vreeland Oscillator[1] generates alternating currents having a pure sinusoidal character and a constant but controllable frequency. Morgan and Lammert[2] were " amazed " to find that the frequency of the Vreeland oscillator is not so constant as was assumed. Changes of 1 per cent occurred in runs, probably owing to change of capacity of the condensers with temperature—a source of error which, it may be remarked, is also present in other types of work of supposedly high accuracy where ratio-type condensers are used.[3]

The use of a direct current with a rotating commutator and galvanometer has been recommended:[4] when it is used, the resistance must remain constant when the speed is varied, or the ratio arms of the bridge changed by a constant multiple. Hall and Adams and Miller[5] used the thermionic valve as a generator of current of high frequency. The connections are shown in Fig. 5. The condensers C_1 and C_2 control the frequency, one being of small capacity and continuously variable and the other variable in steps of 0.005 microfarad. "Generators of this type may be made to yield a current of from a few tenths of a milliampère or less to 25 ampères and with a frequency varying from half a cycle per second to 50 million cycles per second." At frequencies below 1000 cycles, a troublesome first harmonic is present. The arrangement for amplification, when a very weak current is sent through the cell, is shown in Fig. 6.[6]

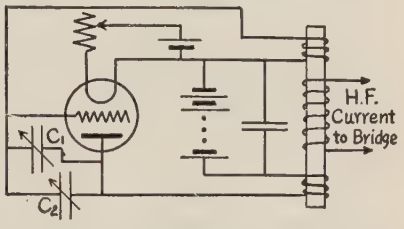

Fig. 5. Thermionic Valve Connections for Conductivity Measurements

Current Detector: The most satisfactory instrument[7] for the detection of alternating current in bridge measurements is the telephone,[8] introduced by

[1] Leeds and Northrup Catalog No. 48 (1919), p. 14 f.; Kraus and Parker, *J. Am. Chem. Soc.*, **44**, 2429 (1922).

[2] *J. Am. Chem. Soc.*, **48**, 1220 (1926).

[3] Partington and Shilling, *Phil. Mag.*, **6**, 920 (1928).

[4] MacGregor, *Trans. Roy. Soc. Canada*, **1**, 21 (1882); Fitzpatrick, *Brit. Ass. Rep.*, p. 328 (1886); Whetham, *Phil. Trans.*, **194**, 321 (1900); Pfleiderer, *Z. Elektrochem.*, **19**, 925 (1913).

[5] *J. Am. Chem. Soc.*, **41**, 1515 (1919); Jones and Josephs, *ibid.*, **50**, 1049 (1928); Ulich, *Z. physik. Chem.*, **115**, 377 (1925); Wagstaffe, *Phil. Mag.*, **47**, 66 (1924); Randall and Scott, *J. Am. Chem. Soc.*, **49**, 637 (1927); Burton and Pitt, *Phil. Mag.*, **5**, 939 (1928); Woolcock and Rust, *ibid.*, 1130.

[6] Lorenz and Klauer, *Z. anorg. Chem.*, **136**, 121 (1924). On sensitivity of telephones see Washburn, *J. Am. Chem. Soc.*, **39**, 235 (1917).

[7] Theory and descriptions of thermionic valves: De Forest, *Electrician*, **73**, 842 (1914); *Electr. World*, **65**, 465 (1914); Langmuir, *Phys. Rev.*, **2**, 450 (1913); *Gen. Electr. Rev.*, (May), 327 (1915); Armstrong, *Electr. World*, **64**, 1149 (1914); Van der Bijl, *Phys. Rev.*, **12**, 171 (1918); Latour, *Electrician*, **78**, 280 (1916); *Circular Bur. Stand.*, **74**, 200 (1918); Fleming, *Proc. Roy. Inst.*, **23**, 161 (1923).

[8] Washburn and Parker, *J. Am. Chem. Soc.*, **39**, 235 (1917): a precision of 1 in 10^7 can be attained with a telephone with an audibility current of 10^{-9} amp., which is reached in telephones of moderate price. Tuning to the frequency of the current is discussed. See also Rayleigh, Phil. Mag., 1894, **38**, 285, 295. Flat type 'phones with adjustable magnets are now obtainable.

Kohlrausch. For ordinary work the writer finds the old long Bell telephone usually much better than the flat type. The choice of a good telephone is essential, and some slight adjustment is often required. A common trouble is iron particles between the disc and magnets. Absolute vanishing of the sound is never attained, but a well-defined minimum should be got if all is in order. The resistance of the telephone may be about 10 ohms or less, and the remaining resistances adjusted accordingly. The use of electrodynamometers and vibration galvanometers [1] has been recommended.

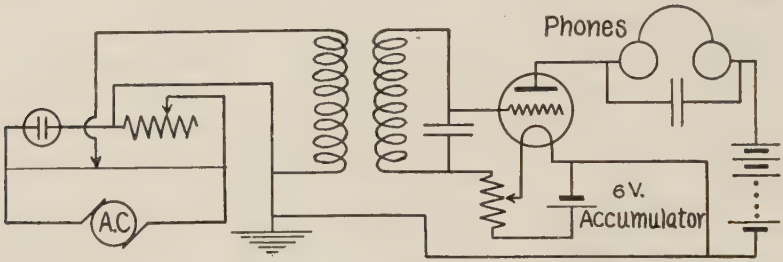

FIG. 6. Experimental Arrangement for Weak Currents

Resistance Bridge: A Wheatstone bridge arrangement of ordinary type may be used. For ordinary work a simple stretched wire of constantan or platinum-iridium, with a knife-edge tapping contact, is sufficient. The coil and telephone are connected with a plug resistance box as known resistance, and the cell, as in Fig. 7. The wire may also be wound on an ebonite or marble drum, with a wheel contact.[2] The wire must be carefully calibrated.[3] Dial resistance boxes are convenient. Nernst [4] recommends the use of standard liquid resistances of negligible temperature coefficient to balance the electrolytic cell, when the bridge arrangement is more symmetrical and sharper readings are obtained. The solution contains 121 grams of mannitol, 41 grams of boric acid, and 0.06 gram of potassium chloride per litre. Its conductivity at 18° is 0.00097 ohm.[5]

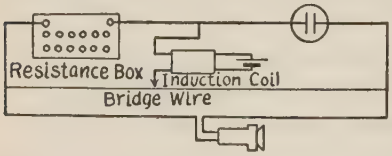

FIG. 7. Experimental Arr ngement for Conductivity Measurements

[1] Kohlrausch, Leitvermögen, p. 30 f.; Thiessen, *Z. Elektrochem.*, **30**, 473 (1924).

[2] Kohlrausch, *Ann. Physik*, **11**, 653 (1880); **56**, 177 (1895); Leitvermögen, p. 41.

[3] Kohlrausch, Leitvermögen, p. 45. See also, for precision bridges, Leeds and Northrup Catalog No. 48 (1919), p. 21 f.

[4] *Z. physik. Chem.*, **14**, 622 (1894); Magnanini, *ibid.*, **6**, 58 (1890).

[5] On such solutions see numerous papers by Boeseken and co-workers: *Proc. K. Akad. Wetens. Amsterdam*, **15**, 216 (1912); *Rec. Trav. Chim.*, **30**, 392 (1911); **34**, 96, 272 (1915); **35**, 211, 309 (1916); **36**, 167 (1916); *Proc. K. Akad. Wetens. Amsterdam*, **18**, 1647 (1916); **21**, 907 (1919); *Rec. Trav. Chim.*, **37**, 130, 144, 162, 165, 179 (1918); **39**, 178 (1920); **40**, 568, 574 (1921); and later; Hermus, *Z. anorg. Chem.*, **142**, 111 (1925).

If resistance coils are used they should be bifilar wound so as to neutralize self-inductance, but as this introduces considerable capacity in large coils (1000 ohms and over), the latter (only) should be wound by Chaperon's method,[1] i.e., in simple layers but each layer in the reverse sense to the preceding. The box should have coils of, say, 30, 70, 200, 700, 2000 and 7000 ohms. The resistance taken from the box should bring the slider to about the middle of the bridge wire in making the balance. If an electrodynamometer is used, one coil is put in series with the induction coil, and the other diagonally across the bridge.[2]

The method of carrying out the conductivity measurement is simply to adjust the resistance in the arm opposite the cell till the minimum sound is heard in the telephone. The bridge is then regarded as balanced. The sources of error in Kohlrausch's method have been studied by Washburn and Bell,[3] and an improved technique for solutions between 0.001 *n*. and 0.000001 *n*. evolved. A high frequency generator replaces the coil, and special resistance units in the box are made by sealing platinum wires into the ends of a glass rod and connecting them by a film of platinum deposited on the glass. A tuned telephone and an extended bridge wire are used, all measurements being made about the middle of the bridge. The precision reached with all solutions from pure water to 6 *n*. was 0.01 per cent, which can be extended to 0.001 per cent with care in most cases. In a later paper,[4] it is stated that an induction coil has a unidirectional component, and its time integral is not zero, leading to some polarization; it is also impossible to keep the frequency constant. A telephone tuned to the frequency used [5] must also be employed: various methods of tuning (mechanical, electrical and acoustical) are described. The paper condensers used by Kohlrausch (see later) are unsuitable for very accurate work. They are replaced by air or mica condensers.[6] A frequency of about 1000 per sec. is recommended.

A very comprehensive account of the bridge assembly, making use of value oscillator circuits, is described by Jones and Josephs.[7] The bridge assembly for precision work is also described by Morgan and Lammert.[8]

Conductivity Water: Very pure water is essential for conductivity work. The same applies, of course, to other solvents used. The purest water was obtained by Kohlrausch and Heydweiller[9] and had a specific conductance of only 0.043×10^{-6} ohm^{-1} at 18°, but very special precautions had to be used to obtain only a few cc. of this water, and the operation has never been repeated

[1] *Compt. rend.*, **108**, 799 (1889); *J. de Phys.*, **9**, 481 (1890); Curtis and Grover, *Bull. Bureau Stand.*, **8**, 514 (1911) (improved method).

[2] Cf. Acree and Taylor, *J. Am. Chem. Soc.*, **38**, 2403, 2415 (1916).

[3] *J. Am. Chem. Soc.*, **35**, 177 (1913).

[4] Washburn, *J. Am. Chem. Soc.*, **38**, 2431 (1916).

[5] *Ibid.*, **39**, 235 (1917). Cf Thiessen, *Z. Elektrochem.*, **30**, 473 (1924).

[6] Leeds and Northrup Catalog No. 48 (1919), p. 5.

[7] *J. Am. Chem. Soc.*, **50**, 1049 (1928)

[8] *J. Am. Chem. Soc.*, **48**, 1220 (1926).

[9] Kohlrausch, *Ann. Physik Egänzungsbd.*, **8**, 1 (1878); Kohlrausch and Heydweiller, *Ann. Physik*, **53**, 209 (1894); Kohlrausch, *Z. physik. Chem.*, **42**, 193 (1902).

with success since.[1] Water was distilled backwards and forwards forty-two times in a vacuum at a low temperature, and collected directly in a glass conductivity cell which had been kept ten years filled with conductivity water to remove traces of soluble matter from the glass.

In air, the conductivity of the best water rises to at least 0.7×10^{-6}, chiefly owing to dissolved carbon dioxide, and a good water for general use may be taken as one about 1×10^{-6}.

According to Kraus and Parker [2] correct results cannot be obtained with solutions of *acids* in such water, in glass cells, at concentrations below 0.001 *N*. Water prepared and stored in an atmosphere of purified air may be got down [3] to 0.06×10^{-6}.

A very large number of methods of preparing conductivity water have been proposed.[4] A convenient laboratory still for conductivity water is the pan still of Bousfield.[5]

The water is kept in steamed-out glass bottles or porcelain vessels; [6] bottles coated inside with melted paraffin wax have been recommended. The temperature coefficient of conductivity water is about 2 per cent per 1° C.

The Water Correction: The correction of the measured value of the conductivity for the conductivity of the water has already been mentioned. The water correction has been discussed by Kendall,[7] who concluded that if chemically pure water were available no correction would be required. Washburn [8] does not agree; even with water of conductivity 0.04×10^{-6} the correction is 0.3 per cent at 0.0001 *n*. and that at 0.00001 *n*. is 3 per cent. With 0.06×10^{-6} water the corrections are not much larger. The advantage of ultrapure water is not the elimination of the water correction but elimination of uncertainty as to the appropriate method of applying the correction.

When very pure water stands exposed to air it dissolves carbon dioxide and its conductivity rises, at first rapidly, then more slowly, until a maximum is reached at about 0.8 to 1.0×10^{-6}, when the water is in equilibrium with the carbon dioxide in the atmosphere.[9] This may be called "equilibrium

[1] Nernst informed the writer that he had made unsuccessful attempts.

[2] *J. Am. Chem. Soc.*, **44**, 2429 (1922).

[3] Washburn, *J. Am. Chem. Soc.*, **40**, 109 (1918).

[4] Summary in Kendall, *J. Am. Chem. Soc.*, **38**, 2460 (1916); Jones and Mackay, *Z. physik. Chem.*, **22**, 237 (1897); Hantzsch and Barth, *Ber.*, **35**, 210 (1902); Hulett, *Z. physik. Chem.*, **21**, 297 (1896); Lorenz, *ibid.*, **82**, 612 (1913); MacGregory, *Ann. Physik*, **51**, 126 (1894); Nernst, *Z. physik. Chem.*, **8**, 110 (1891); Ostwald, *Ann. Physik*, **40**, 735 (1890); Paul, *Z. Elektrochem.*, **20**, 179 (1914); Pfeiffer, *Ann. Physik*, **31**, 831 (1887); Schick, *Z. physik. Chem.*, **42**, 157 (1903); Kraus and Dexter, *J. Am. Chem. Soc.*, **44**, 2468 (1922); Hartley, Campbell and Poole, *J. Chem. Soc.*, **93**, 428 (1908); Thole, *ibid.*, **101**, 207 (1912); Bourdillon, *ibid.*, **103**, 791 (1913); Clevenger, *J. Ind. Eng. Chem.*, **11**, 964 (1919); Kendall, *J. Chem. Soc.*, **101**, 1275 (1912).

[5] *J. Chem. Soc.*, **87**, 740 (1905); **101**, 1443 (1912). The tin tube when soldered is useless.

[6] Kohlrausch, Leitvermögen, 115 ff.

[7] *J. Am. Chem. Soc.*, **38**, 1480, 2460 (1916); **39**, 7 (1917); Remy, *Z. Elektrochem.*, **31**, 88 (1925).

[8] *J. Am. Chem. Soc.*, **40**, 109 (1918).

[9] Kohlrausch, *Ges. Abh.*, **2**, 871; Kendall, *J. Am. Chem. Soc.*, **38**, 1480, 2464 (1916).

water." If solutions are to be exposed to the air, such water is better than the purest water as far as constancy of conductivity is concerned, but equilibrium water is just as difficult to maintain at a constant conductivity as the purest water.[1]

Washburn has described methods of correcting for the dissolved carbon dioxide and for salts, but he emphasizes [2] that some uncertainty attaches to the correction on account of: (i) the magnitude of the correction; (ii) the proportion of conductivity due to CO_2; (iii) the nature of the products of hydrolysis and other impurities than CO_2; (iv) difficulty of keeping the water constant in composition. He points out that his results are not in agreement with those of Arrhenius,[3] who found that the carbonic acid correction for the salt of a strong acid and base (sodium chloride) dissolved in equilibrium water at 18° is negative in sign, starting at zero for high dilutions, reaching a largest value of − 0.1 per cent at 0.0001 $n.$, and then falling away to zero at higher concentrations, whereas Washburn's correction is positive in sign and should increase continuously with dilution, reaching a maximum value of only + 0.016 per cent at high dilutions. This refers to carbonic acid as the only impurity and the equation is:

$$P_m = 1.15 \times 10^5 \alpha k_w / \Lambda_{H_2CO_3} K_e,$$

where P_m = percentage correction to be added to the conductivity (specific) after the usual water correction has been applied, viz., to κ (solution) − κ_0 (water); k_w = specific conductance of the water; $K_e = \alpha^2 c/(1 - \alpha)$ for the salt; $\Lambda_{H_2CO_3}$ = equivalent conductivity of H_2CO_3. E.g., with 0.00005 $n.$ KCl, $K_e = 0.0210$; $\alpha = 1$; $\Lambda_{H_2CO_3} = 353$; hence if $k_w = 1 \times 10^{-6}$, $P_m = 0.016$ per cent.

If saline impurities are present also, the correction is larger, and Washburn proposes a total correction of Kohlrausch's data of + 0.02 per cent at 0.0001 $n.$ and 0.0002 $n.$; of + 0.01 per cent for 0.0005 $n.$, and 0.001 $n.$, and no correction for higher concentrations. The corrections for salts of weak acids and bases, and for salts of higher valence types, are regarded as problematical.

Errors in Conductance Measurements: The influence of temperature on conductance amounts to about 2 per cent per 1° C., so that, to obtain an accuracy of 0.1 per cent, temperature control to 0.05° is necessary, i.e., a thermostat must be used. The Lowry bulb regulator filled with toluene, with an electrical mercury contact operating a relay and heating lamp, with good stirring, gives excellent results, especially if the capillary stem is prolonged inside the wider top by a capillary tube fitted in with a little cement, inside which capillary tube fits the platinum wire cut-out. The toluene may be purified by refluxing with 1 per cent sodium amalgam, washing with water and redistilling: a small amount of water comes over first. The toluene has then

[1] Kohlrausch, *loc. cit.*, p. 996.

[2] *J. Am. Chem. Soc.*, **40**, 109 (1918); Walden and Ulich, *Z. Elektrochem.*, **34**, 25 (1928).

[3] *Medd. K. Vetensk. Akad. Nobelinst.*, no. 42, **2**, p. 10 (1913); Kendall, *J. Am. Chem. Soc.*, **39**, 15 (1917).

no action on the mercury in the regulator.[1] A convenient ice-bath for determinations at 0° has been described.[2] The thermometer is placed alongside the cell and ample time allowed to attain temperature equilibrium. The current from the induction coil heats the liquid in the cell and it should not be kept running for long. The best way to reduce the current from the coil is to insert resistance in the primary circuit as long as the hammer break still works, otherwise a very large resistance is necessary in the secondary circuit, from one pole of the coil; but, this may cause trouble by static charging of the telephone unless the other pole of the coil is earthed.

The resistance of the leads from the cell to the bridge may be found with mercury in the cell, and should be subtracted from all measurements.[3]

With an alternating current of sufficiently high frequency, and the electrodes well platinized, polarization is practically eliminated. Elimination of polarization is effected [4] by (*a*) platinizing and increase of frequency; (*b*) compensation and increase of frequency. It can always be eliminated by the usual process of platinizing even when comparatively low frequencies (not greater than 1000) are used. The decomposing action of platinum black on the solution may, however, set a limit to this method, in which case, if the solution is not too concentrated, polarization may be eliminated by simply increasing the frequency. Taylor and Acree [5] extrapolate from frequencies of 500, 750, 1000 and 1500, obtained by the Vreeland Oscillator, to infinite frequency. They also use the formula

$$(R_f - R_\infty)/L_f f = \text{const.},$$

where R and L are resistance and inductance, f is the frequency; and they also show that capacity does not depend on a gas layer on the electrodes. A conductivity cell acts as a resistance in series with a simple condenser with a leak. Eastman [6] considers that the conductivity is smaller at zero frequency than in the range immediately above zero. His measurements show a difference of only 0.02 to 0.03 per cent with direct current and with 1000 cycles alternating, but he considers this difference is in the right direction. Haworth [7] considers that extrapolation to infinite frequency gives the right resistance. The resistance is independent of frequency if the potential measuring electrodes are not in the main current stream.

The effect of polarization is not merely to reduce the sharpness of the minimum but also to shift the center of this;[8] its effect is not simply a pure

[1] Beal and Southern, *J. Am. Chem. Soc.*, **49**, 1994 (1927).

[2] Parker and Parker, *J. Am. Chem. Soc.*, **46**, 312 (1924).

[3] Washburn, *J. Am. Chem. Soc.*, **39**, 235 (1917), recommends enclosing the leads, kept straight and parallel, in an earthed metal sheath.

[4] Nernst, *Z. physik. Chem.*, **14**, 622 (1894); Déguisne, *Diss.*, Strasburg (1895); Washburn, *J. Am. Chem. Soc.*, **38**, 2456 (1916).

[5] *J. Am. Chem. Soc.*, **38**, 2415 (1916); Kraus and Parker, *ibid.*, **44**, 2422 (1922).

[6] *J. Am. Chem. Soc.*, **42**, 1649 (1920).

[7] *Trans. Farad. Soc.*, **16**, 365 (1920); Banerji, *ibid.*, **22**, 111 (1926); Becker, *Z. Elektrochem.*, **32**, 305 (1925).

[8] Wien, *Ann. Physik*, **47**, 626 (1892).

condenser reactance, but an increase of effective resistance accompanies it, which is smaller with large electrodes [1] and higher frequency. This is attributed to dissipation of energy owing to the incompletely reversible electrode reaction. Washburn [2] suggests that this points to some catalytic activity of the platinum black. Curtis and Taylor [3] tested Wien's method of electrically compensating for condenser reactance by inserting a variable pure inductance, and find that it gives results within 0.02 per cent of those with platinized electrodes.

Self-inductance (mainly of the bridge coils) and electrostatic capacity in the bridge arms may arise with alternating currents, and it would be difficult to estimate and allow for them. Fortunately, when they are present, there is a want of sharpness in the telephone minimum, and as long as good readings are obtained it may be assumed that inductance, capacity and polarization are negligible, unless the resistances to be measured are very large or very small. The effect of the three sources of error are summarized in the following table: [4]

	Self Induction large when	Polarization large when	Capacity large when
Frequency is	great	small	great
Resistance is	small	small	great

The frequency in the circuit is much higher than that of the hammerbreak of the coil.[5]

Capacity is appreciable in bifilar wound coils, and these should not be used of resistance greater than 500 ohms; higher units should have Chaperon winding. The effect of capacity is appreciable when a liquid of higher resistance is in the cell; it is also present owing to the water in the thermostat acting as a conducting coating of a Leyden jar. This may be got over by immersing the cell in a vessel of paraffin oil [6] or using oil in the thermostat.[7] A small condenser, e.g., of tinfoil on glass, sliding between similar plates, or tinfoil between paraffined paper, may also be inserted in parallel with the bridge arm opposite the one in which capacity occurs and varied till the minimum is sharp. A condenser in series with a circuit can balance inductance when $f = 1/2\pi\sqrt{LC}$; f = frequency, L = inductance, C = capacity. If corresponding inductance and capacity are present, the circuit behaves as a non-inductive one.[8]

[1] Wien, *Ann. Physik*, **58**, 37 (1896); Neumann, *ibid.*, **67**, 499 (1899). Haworth, *loc. cit.*, has overlooked this.

[2] *J. Am. Chem. Soc.*, **38**, 2459 (1916).

[3] *Phys. Rev.*, **6**, 61 (1915); Wolcott, *Ann. Physik*, **12**, 653 (1903).

[4] Lehfeldt, Electrochemistry, London (1908), p. 57; Kohlrausch, Leitvermögen, p. 55 f.; Washburn, *J. Am. Chem. Soc.*, **38**, 2431 (1916); Kruger, *Z. physik. Chem.*, **45**, 1 (1903); Oberbeck, *Ann. Physik*, **19**, 625 (1883); **21**, 139 (1884); Schlesinger and Read, *J. Am. Chem. Soc.*, **41**, 1727 (1919); Wien, *Ann. Physik*, **58**, 37 (1896); **59**, 267 (1896).

[5] Lenard, *Ann. Physik*, **39**, 619 (1890).

[6] Kohlrausch, *Ann. Physik*, **49**, 225 (1893); Leitvermögen, p. 59.

[7] Jones and Josephs, *J. Am. Chem. Soc.*, **50**, 1049 (1928).

[8] Taylor and Acree, *J. Am. Chem. Soc.*, **38**, 2403 (1916), find agreement to 0.001 per cent with (*a*) inductance, (*b*) condenser, used to balance the capacity of the conductivity

Equivalent Conductance at Infinite Dilution: The value of Λ for an electrolyte is found experimentally to increase with dilution and to approach a limiting value which is reached at different dilutions for different types of electrolytes and is known as the limiting value of the equivalent conductance for infinite dilution, Λ_∞, or for zero concentration, Λ_0. In the light of the electrolytic dissociation theory the interpretation of Λ_∞ is clear: it refers to complete ionization. The kind of increase of Λ with dilution is shown in the following table (Kohlrausch):

TABLE IV

Λ_φ AT 18° C.

Dilution φ in cc.	KCl	$\frac{1}{2}CuSO_4$	CH_3COOH
10^3	98.3	25.8	1.32
10^4	112.0	43.9	4.60
10^5	122.4	71.7	14.3
10^6	127.3	98.5	41.0
10^7	129.1	110.0	107.0

It is evident that, in the case of KCl, the limiting value can be calculated with some accuracy by extrapolation; in the case of $\frac{1}{2}CuSO_4$ the approach to a limiting value is apparent, but this cannot be calculated by extrapolation from the figures given; in the case of acetic acid it is evident that, even at high dilutions, the limiting value is far from being attained. In the case of weak electrolytes, such as acetic acid, the limiting value can be found only by indirect methods as explained later.

For the purposes of interpolation and extrapolation the values of Λ at different concentrations are plotted against the cube root, square root or logarithm of the concentration. The first method is used by Kohlrausch,[1] and the curves in Fig. 8 show the results with some typical electrolytes and the character of the extrapolation may be seen. For very dilute solutions Λ may be plotted against the square root of the concentration. The objection to Kohlrausch's method is that it assumes a certain relation between Λ and the concentration which may not hold at very high dilutions.

The Λ curves of acids and bases are more difficult to extrapolate than those of salts, on account of the greater influence of impurities (CO_2, NH_3) in the water, at high dilutions. The curves then exhibit maximum values of Λ at high dilutions, and then fall off rapidly.[2]

cell. Technical methods of measuring conductivity: Keeler, *Trans. Am. Electrochem. Soc.*, **38**, 113 (1920).

[1] *Ann. Physik*, **26**, 161 (1885); **50**, 385 (1893); Liebenow, *Z. Elektrochem.*, **8**, 933 (1901); Kohlrausch and Maltby, *Wiss. Abhandl. P. T. Reichsanstalt*, **3**, 157 (1900).

[2] Whetham and Paine, *Proc. Roy. Soc.*, **81**, 58 (1908); Whetham, *Phil. Trans.*, **194**, 353 (1900); Kendall, *J. Am. Chem. Soc.*, **39**, 12 (1917); Washburn, *ibid.*, **40**, 122 (1918); Chittock, *Proc. Camb. Phil. Soc.*, **15**, 55 (1909). Some solutions exhibit a maximum specific conductance at a certain concentration; this is due to the interplay of ionization and con-

Ostwald's Rule: An empirical relation discovered by Ostwald [1] states that $\mu_{1024} - \mu_{32} = 10.y_+.y_-$, where μ_{1024} and μ_{32} are molar conductances at dilutions

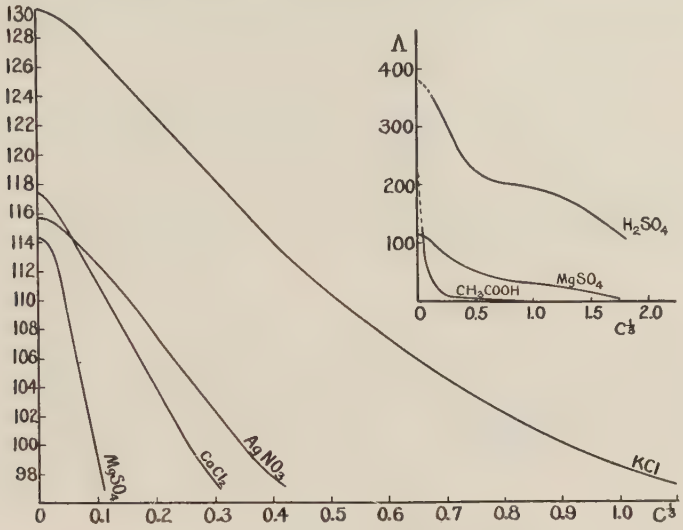

FIG. 8. $\Lambda - C^{1/3}$ Curves

of 1024 and 32 *liters*, respectively, of salts of strong acids or bases, and y_+ and y_- the valencies of the kation and anion. The rule holds very approximately to $y = 6$ and is often useful in finding the basicity of acids or bases ($y_+ = 1$ and $y_- = 1$, respectively).[2]

On the basis of this rule, Bredig (*loc. cit.*) compiled the following table,

TABLE V

CONDUCTANCE CALCULATIONS FOR INFINITE DILUTION

	Dilution (liters per mol.)					
$y_+ \cdot y_-$	32	64	128	256	512	1024
1	15	11.7	8.5	6.4	4.2	3.2
2	(26.6)	22.3	17	12.7	8.5	6.4
3	(39.3)	31.8	24.4	18	12.7	8.5
4	(55)	44.6	33	24.4	17	10.6
5	(66)	56.3	41.5	30.8	22.3	13.8
6	(75.5)	(63.8)	51	38.3	26.6	17

centration: sulphuric acid at 30 per cent (Kohlrausch and Holborn, Leitvermögen, p. 75); hydrochloric acid 18 per cent (Gibson, *Trans. Roy. Soc. Edinb.*, **48**, 117 (1912)); magnesium sulphate (Kohlrausch and Holborn, *loc. cit.*, p. 76).

[1] *Z. physik. Chem.*, **1**, 74 (1887); **2**, 840 (1888); Walden, *ibid.*, **1**, 529 (1887); **2**, 49 (1888); Bredig, *ibid.*, **13**, 191 (1894).

[2] On methods of making up to these dilutions see Klemenc, *Chem. Z.*, **35**, 1420 (1911).

giving the values to be added to the molar conductance of a salt at 25° at the given dilution to make up μ_∞. The accuracy is usually about one unit, and the table is useful for approximate work. The first column gives $y_+ . y_-$. E.g., for KCl, this is 1×1; for $BaCl_2$, 2×1; for $Al_2(SO_4)_3$, it is $(3 \times 2 = 6)$. Bracketed values are less certain. (Conductances are in ohm^{-1}, not Siemens' units.)

This table, of course, can be used only for approximation;[1] the values calculated from the higher dilutions are often higher than those found from the lower dilutions.

Calculation of Λ_∞: The extrapolation of Λ to infinite dilution is a matter of importance. Kohlrausch, as mentioned, extrapolated by plotting Λ against $c^{1/3}$, assuming [2]

$$\Lambda = \Lambda_0 - ac^{1/3} \qquad \text{or} \qquad \Lambda = \Lambda_\infty - a\varphi^{-1/3}.$$

The value of a varies from one salt to another, but it has, at 18°, approximately the value 400 for uni-univalent electrolytes. An accuracy of only 1 per cent. is claimed.[3] At the highest dilutions a better approximation is given, according to Kohlrausch,[4] by the equation

$$\Lambda = \Lambda_0 - bc^{1/2}$$

(for c from 0.002 or 0.005 to 0 equiv. per liter).

Lorenz [5] gives values of a and b for basic organic kations (110 substances) for which both formulae apply equally well: $\mu_\infty - \mu = 91.54c^{1/2}$; $\mu_\infty - \mu = 58.2c^{1/3}$. The equation with $c^{1/2}$ is said by Kohlrausch to be "surprisingly exact." For higher concentrations (to 0.1 *n*.) he proposes [6]

$$\Lambda_0 - \Lambda = B\Lambda^p c^{1/2},$$

with another constant p, varying from substance to substance. This does not hold for bi-bivalent electrolytes. For concentrated solutions Gibson [7] proposes $\Lambda' = \Lambda_0 - Dc'$, where

$$\Lambda' = \kappa/c',$$

[1] Lorenz, *Z. anorg. Chem.*, **108**, 81 (1919); Lorenz and Posen, *ibid.*, **96**, 90 (1916); Wegscheider, *Z. Elektrochem.*, **18**, 277 (1912).

[2] Leitvermögen, p. 107; *Ann. Physik.*, **26**, 161 (1885); **50**, 385 (1893); *Berl. Bers*, ii, 1002 (1900); *Z. Elektrochem.*, **13**, 333 (1907); Kohlrausch and Steinwehr, *Berl. Ber.*, i, 581 (1902); Hertz, *Ann. Physik.*, **37**, 1 (1912), deduced the equation $\Lambda_0 - \Lambda = f(c^{1/3})$, whence by a suitable adjustment of co-ordinates all electrolytes could be represented on a single curve; Lorenz, *Z. anorg. Chem.*, **113**, 135 (1920); Lorenz Neu, *ibid.*, **116**, 45 (1921); Lorenz and Michael, *ibid.*, **116**, 161 (1921); Lorenz and Ostwald, *ibid.*, **114**, 209 (1920) and Lorenz and Voigt, *ibid.*, **145**, 277 (1925) find that the constants are not independent of the nature of the electrolyte as required by Hertz's theory, but have specific values for each ion.

[3] The same equation was put forward by A. W. Porter, *Trans. Farad. Soc.*, **15**, 122 (1919), it holds very approximately for $ZnCl_2$ and Na_2SO_4 as well as for LiCl.

[4] *Loc. cit.*, p. 108; Bousfield, *J. Chem. Soc.*, **103**, 307 (1913); Davies, *J. Phys. Chem.*, **29**, 473 (1925) proposes $\Lambda_0 - \Lambda = k\sqrt{c\Lambda_0}$ below 0.002 *N*.

[5] *Z. anorg. Chem.*, **108**, 81, 191 (1919).

[6] Leitvermögen, p. 108; Lorenz, *Z. anorg. Chem.*, **108**, 81, 191 (1919).

[7] *Trans. Roy. Soc. Edinb.*, **45**, 241 (1906).

c' being the concentration in equivalents per *gram* of *solution*. This does not hold for dilute solutions, and cannot be used for extrapolation to Λ_0.

Randall [1] finds that if the percentage ionizations of salts are plotted against $c^{1/2}$ the curves fall into non-intersecting groups according to the valence types of the salts. Salts of the same valence type also divide themselves into distinct groups, e.g., halides of alkali metals and ammonium,[2] and, in this case, $\alpha = \Lambda/\Lambda_0$ becomes more nearly equal as zero concentration is approached. If α, Λ, and Λ_0 are known for one salt of a group, α may be assumed the same at a given concentration for another member, and thus, if Λ is known, Λ_0 may be calculated from α. The values of Λ_0 so found for different concentrations are then plotted against $c^{1/2}$ and extrapolated to zero concentration to give a final value of Λ_0. A method similar to that of Kohlrausch was used by A. A. Noyes and his collaborators.[3]

Ostwald's Dilution Law: Consider the ionization of a binary electrolyte:

$$\underset{1-\alpha}{AB} \rightleftharpoons \underset{\alpha}{A'} + \underset{\alpha}{B'}.$$

If the volume of solution is V, and if α is the degree of ionization, the concentrations are: $[AB] = c_0 = (1 - \alpha)/V$; $[A'] = [B'] = c_1 = \alpha/V$. The law of mass action then gives: $c_1^2/c_0 = \text{const.} = K$, i.e.,

$$\alpha^2/(1 - \alpha)V = K. \tag{1}$$

Since $\alpha = \Lambda/\Lambda_\infty$, we find also:

$$\Lambda^2/\Lambda_\infty(\Lambda_\infty - \Lambda)V = c\Lambda^2/\Lambda_\infty(\Lambda_\infty - \Lambda) = K.$$

This equation is known as Ostwald's Dilution Law.[4] Its deduction depends on the assumptions that the solution is dilute, and that the law of mass action can be applied to charged ions.[5]

Experimental investigation of the conductivities of dilute solutions of weak organic acids [6] and weak organic bases [7] showed that the law was very

[1] *J. Am. Chem. Soc.*, **38**, 788 (1916).

[2] This was well known to Kohlrausch, Leitvermögen, p. 108.

[3] Noyes and Falk, *J. Am. Chem. Soc.*, **34**, 462 (1912).

[4] *Z. physik. Chem.*, **2**, 36 (1888).

[5] The disturbing effects of increasing concentration and increasing ionization may act in opposite directions. Wegscheider, *Z. physik. Chem.*, **69**, 603 (1909), assumes that the law holds up to concentrations of 0.03 *n.*; Wegscheider and Lux, *Monatsh.*, **30**, 411 (1909), find agreement with salts of α-naphthalenesulphonic and p-toluenesulphonic acids up to 0.006 *n.* Drucker, Tarle and Gomez, *Z. Elektrochem.*, **19**, 8 (1913), find that KBr obeys Ostwald's dilution law up to 0.01 *n.* Drucker, *ibid.*, **18**, 562 (1912), finds that $N(CH_3)_4Cl$ and $N(CH_3)_4Br$ obey the law up to 0.02 *n.* Holmberg, *Svensk. Kem. Tidskr.*, p. 6 (1918), thinks NaI obeys the law up to 0.05 *n.*, but he did not use conductivity methods. Washburn and MacInnes, *J. Am. Chem. Soc.*, **33**, 1686 (1911), consider that the law holds only at much higher dilutions, in the case of strong electrolytes. In the case of weak electrolytes it probably holds up to about 0.1 *n.* Cf. Jones and White, *Am. Chem. J.*, **42**, 520 (1909); Jones and Wightman, *ibid.*, **46**, 56 (1911).

[6] Ostwald, *Z. physik. Chem.*, **3**, 170, 241 (1889).

[7] Bredig, *Z. physik. Chem.*, **13**, 289 (1894); Goldschmidt and Salcher, *ibid.*, **29**, 89 (1899).

satisfactorily followed. The results for acetic acid are given in Table VI, the data being from Rivett and Sidgwick,[1] and Kendall.[2]

TABLE VI

ACETIC ACID IN AQUEOUS SOLUTION AT 25°

V = Vol. in liters of solution containing 1 mol. CH_3CO_2H.
Λ = Equivalent conductivity, in Kohlrausch units = specific conductivity/concentration in mol. per cc.
d = Density of solution (water = 1).
η = Viscosity of solution (water = 1).
α = Ionization = Λ/Λ_∞; $\alpha' = \eta\Lambda/\Lambda_\infty\eta_\infty$.

V	Λ	α	$K \times 10^6$	d	η	α'	$K' \times 10^6$	$K'' \times 10^6$
0.334	0.6186	0.001595	7.7	1.0235	1.347	0.002149	13.9	16.5
0.672	1.123	0.002896	12.5	1.0122	1.169	0.003385	17.2	18.6
0.989	1.443	0.003636	14.0	1.0084	1.112	0.004043	17.4	18.4
1.977	2.211	0.005701	16.5	1.0043	1.056	0.006020	18.3	18.8
5.374	3.804	0.009806	18.1	1.0017	1.021	0.01001	18.8	19.0
10.753	5.361	0.01382	18.0	1.0009	1.010	0.01396	18.4	18.5
24.875	8.388	0.02163	19.2	1.0004	1.004	0.02172	19.5	19.5
63.26	13.03	0.03359	18.5	1.0002	1.002	0.03366	18.6	18.6
∞	387.9	1.00000	—	1.0000	1.000	1.00000	—	—

The value of K is calculated from equation (1) above; the value α' is corrected for viscosity: $\alpha' = \eta\Lambda/\Lambda_\infty\eta_\infty$. Kendall (*loc. cit.*) assumes that the ionization involves interaction with water molecules, and writes the mass law in the form:

$$[ion]^2/[salt][water] = K'' = K'.1000d_0/(1000d - m/v),$$

where d_0, d are the densities of pure water and solution, and m = molar weight of solute. The values of K (from α), K' (from α'), and K'' are given in the table, and the constancy of the latter extends even to 3 *n.* concentration. The "uncorrected" law (K) holds below 0.2 *n.* with all the accuracy found in the applications of the law of mass action to any systems, and the dilution law in the case of *weak electrolytes* is a form of the law of mass action which is very closely followed by experiment.[3] In the case of *strong electrolytes* the law fails, as the figures in Table VII demonstrate. It will be seen that the dissociation is nearly complete at all the concentrations given, and it is now generally assumed that the dissociation is really practically complete (over 99 per cent) and that the variation of Λ with concentration is due to other causes.

[1] *J. Chem. Soc.*, **97**, 734 (1910).

[2] *J. Am. Chem. Soc.*, **36**, 1069 (1914).

[3] Cf. MacInnes, *J. Am. Chem. Soc.*, **48**, 2068 (1926), who shows that when the degree of ionisation is calculated by dividing the conductivity by the computed value of the completely ionized acid at the same ion concentration (from the Debye theory) even better results are found; Walden and Ulich, *Z. Elektrochem.*, **34**, 25 (1928)—weak bases.

TABLE VII

POTASSIUM CHLORIDE AT 18° C.

V lit.	Λ	$\Lambda/\Lambda_\infty = \alpha$	$1 - \alpha$	K
∞	129.91	1.0000	0.0000	—
10,000	129.07	0.9936	0.0064	0.0154
5,000	128.77	0.9912	0.0088	0.0223
2,000	128.11	0.9862	0.0138	0.0352
1,000	127.34	0.9802	0.0198	0.0485
500	126.31	0.9723	0.0277	0.0681
200	124.41	0.9577	0.0423	0.1084
100	122.43	0.9424	0.0576	0.1542

Dilution formulae: Any equation connecting Λ, or $\Lambda/\Lambda_\infty = \alpha$, with concentration or dilution $V = 1/c$, so that Λ_∞ may be calculated from one or more values of Λ, is called a dilution formula. Several have been proposed: Ostwald's is the simplest.

Rudolphi [1] $$\alpha^2/(1-\alpha)\sqrt{V} = K$$

van't Hoff [2] $$\alpha^{3/2}/(1-\alpha)\sqrt{V} = K$$

Partington [3] $$\alpha^2/(1-\alpha)(V+\epsilon\alpha) = K$$

Kendall [4] $$\alpha^2/(1-\alpha)V = K + k(1-\alpha)/\alpha$$

Walker [5] $$\alpha^2/(1-\alpha)V = k(1-\alpha)/\alpha$$

Macdougall,[6] and Kraus and Bray

$$\alpha^2/(1-\alpha)V = K + k(\alpha/V)^n$$

Szyszkowski [7] $$\alpha^2/(1-\alpha)V = K + k\{[(1-\alpha)/V]^{1/2}\}^p$$

Ghosh [8] $$ln\frac{\mu_\infty}{\mu_v} = \frac{1}{2RT}\frac{Ne^2\sqrt[3]{2N}}{D\sqrt[3]{V}}$$

[1] *Z. physik. Chem.*, **17**, 385 (1895).

[2] *Z. physik. Chem.*, **18**, 300 (1895); Hughes, *Phil. Mag.*, **42**, 134 (1921); Kohlrausch, *Z. physik. Chem.*, **18**, 662 (1895); Vaubel, *Z. angew. Chem.*, **15**, 395 (1902); Bousfield, *Z. physik. Chem.*, **53**, 266 (1905); *Proc. Roy. Soc.*, **74**, 563 (1905); *Phil. Trans.*, **206**, 101 (1906); *Trans. Farad. Soc.*, **15**, 47 (1919).

[3] *J. Chem. Soc.*, **97**, 1158 (1910); Hughes, *Phil. Mag.*, **42**, 428 (1921).

[4] *J. Chem. Soc.*, **101**, 1257 (1912); *Medd. K. Vet. Nobel Inst.*, **2**, 38 (1913); *J. Phys. Chem.*, **19**, 193 (1915); cf. Szyszkowski, *Medd. K. Vet. Nobel Inst.*, **3**, Nr. 2 (1914); *ibid.* Nr. 41 (1913) (equation 13).

[5] *Brit. Ass. Rep.*, p. 349 (1911).

[6] *J. Am. Chem. Soc.*, **34**, 855 (1912); Kraus and Bray, *ibid.*, **35**, 1414 (1913); **37**, 1315 (1915); *Science*, **35**, 433 (1912); Falk and Noyes, *J. Am. Chem. Soc.*, **34**, 454 (1912); Harkins, *ibid.*, **33**, 1836 (1911).

[7] *Medd. K. Vet. Nobel Inst.*, **3**, Nr. 2 (1914); **3**, Nr. 11 (1916); *Compt. rend.*, **157**, 767 (1913); cf. Kraus, Electrically Conducting Systems, p. 69.

[8] *J. Chem. Soc.*, **113**, 449, 627, 707, 790 (1918); cf. Partington, *Trans. Farad. Soc.*, **15**, 98 (1919); Kraus, *J. Am. Chem. Soc.*, **43**, 2514 (1921); Arrhenius, *Z. physik. Chem.*, **100**, 9

for a binary electrolyte, where N = Avogadro's number, e = charge on electron, D = the electric constant of solvent; V = dilution in cc.; and for a ternary electrolyte.

$$ln\frac{\mu_\infty}{\mu_v} = \frac{1}{3RT}\cdot\frac{3Ne^2}{D\sqrt{3}}\cdot\frac{2\sqrt[3]{2N}}{\sqrt[3]{V}}$$

Storch[1] $$\alpha^2/(1-\alpha)V = k(\alpha/V)^m$$

or

$$\Lambda = \Lambda_0 - bc^n \qquad \text{where } c = 1/V,$$

k, m and n are constants, and $n = m - 1$.

Barmwater[2] $$1 - \alpha = k(\alpha/V)^{1/3}$$

Bousfield[3] (a) $\alpha^{3/2}/(1-\alpha) = Kh^{1/2}$

(b) $\alpha/(1-\alpha) = h^{1/2}\cdot 10^{1-\alpha}/5.37$

where h = no. of mols of water per mol of KCl.

Bates[4] $$\log \Lambda^2 c/\Lambda_0(\Lambda_0 - \Lambda) = \log K + k(c.\Lambda/\Lambda_0)^h$$

for KCl solutions.

Washburn's Method: Λ method of extrapolation of Λ used by Washburn[5] depends on the assumptions (i) that Ostwald's dilution law $c\alpha^2/(1-\alpha) = K$ (a constant) is followed even by strong electrolytes at very high dilution, *i.e.*, $d\ ln\ K/dc = 0$ when $c = 0$, and also (ii) that the curve connecting K and c does not show deviations from the law of mass action which increase with dilution. The values of K are plotted against c for various assumed values of Λ_0, and of the latter those are rejected which cause the curves at high dilutions to assume radical changes in direction (see Fig. 9). In this way, it is

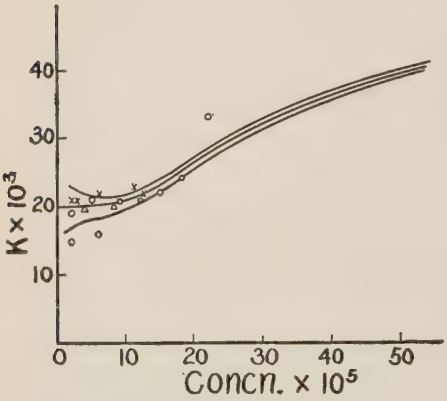

Fig. 9. Washburn's Extrapolation Method

(1922); Kallmann, *ibid.*, **98**, 433 (1921); Prins, *Chem. Weekblad*, **20**, 237 (1923); Chapman and George, *Phil. Mag.*, **41**, 799 (1921); Kendall, *J. Am. Chem. Soc.*, **44**, 717 (1922).

[1] *Z. physik. Chem.*, **19**, 13 (1896); Bancroft, *ibid.*, **31**, 188 (1899); cf. Kohlrausch, *ibid.*, **18**, 662 (1895); *Beibl. Ann. Physik*, **25**, 54 (1901); Georgevics, *Z. physik. Chem.*, **90**, 340 (1915); Bates, *J. Am. Chem. Soc.*, **35**, 519 (1913).

[2] *Z. physik. Chem.*, **28**, 115 (1899); **45**, 557 (1903); **56**, 225 (1906); Walden, *ibid.*, **94**, 374 (1920); Noyes, *J. Am. Chem. Soc.*, **30**, 335 (1908); Hunt, *ibid.*, **33**, 795 (1911).

[3] *Phil. Trans.*, **206**, 155 (1906); *J. Chem. Soc.*, **103**, 307 (1913); *ibid.*, **105**, 1809 (1914).

[4] *J. Am. Chem. Soc.*, **37**, 1431 (1915).

[5] *J. Am. Chem. Soc.*, **40**, 122 (1918); cf. Kendall, *ibid.*, **40**, 622 (1918); **42**, 1077 (1920); Kraus, *ibid.*, **42**, 1 (1920), Properties of Electrically Conducting Systems, 1922, p. 100; Washburn, *J. Am. Chem. Soc.*, **42**, 1090 (1922).

claimed, the value of Λ_0 may be found with an accuracy of 0.01 per cent, provided the conductance data are equally accurate and extend down to 000002 *n*. If the conductance data extend only to 0.0001 *n*., the value of Λ_0 is accurate to about 0.2 per cent.

In an important paper by Arrhenius,[1] in which a correction for the conductivity of the water was applied to Kohlrausch and Maltby's results for the conductivities of potassium chloride, the conclusion was reached that at very high dilutions this electrolyte obeys Ostwald's dilution law, with a value of K, the true dissociation constant, of about 0.024. This occurs with KCl and $NaNO_3$ at dilutions of about 2.10^5 to 4.10^5 liters. The calculation of Arrhenius has been adversely criticized by Washburn,[2] but the results of Washburn and Weiland,[3] with ultra-pure water, appear to conform to Arrhenius's result. The experimental values, from smoothed curves, are given in Table VIII.

TABLE VIII

CONDUCTANCE OF KCl

Temperature 18°. Mol. Wt. KCl = 74.560. Cell constant based on $\kappa = 0.01288$ ohm^{-1} for specific conductance at 25° of a solution of 7.43000 gm. KCl in 1000 gm. solution, weights in air. Conductance to 0.02 per cent.

$c \times 10^3$	$\kappa \times 10^6$	Λ	$\alpha = \Lambda/\Lambda_0$	$K = \alpha^2 c/(1-\alpha)$
0.00	0.0	129.64	1.0	0.020 ± 0.001
0.02	2.5902_2	129.51_1	0.999_{01}	0.020_{02}
0.04	5.1753_6	129.38_4	0.998_{01}	0.020_{06}
*0.06	7.7554_9	129.25_8	0.997_{05}	0.020_{22}
0.08	10.330_9	129.13_8	0.996_{13}	0.020_{50}
0.10	12.902_9	129.02_9	0.9952_9	0.0210_2
*0.30	38.535_3	128.45_1	0.9908_3	0.0321_0
0.40	51.297_6	128.24_4	0.9892_3	0.0363_3
0.60	76.721_4	127.86_9	0.9863_4	0.0427_8
0.80	102.04_1	127.55_1	0.9838_9	0.0480_6
1.00	127.25_8	127.25_8	0.9816_3	0.0524_4

The smallest concentrations used was 7.4945×10^{-6} mol./lit., and the next concentration used was 23.821×10^{-6} mol./lit., so that the results at lower concentrations are mere extrapolations.

Washburn's method suffers from the defect that the assumed law connecting Λ with c at very low concentrations is arbitrarily chosen. It assumes a dilution law which reduces to Ostwald's at very low concentrations.

Ferguson and Vogel's Method: The following method, due to Ferguson and Vogel [4] gives values of Λ_0 for strong electrolytes.

Values of Λ and c are plotted on a curve and values of Λ taken from the

[1] "Die Berechnung des elektrischen Leitungs-vermögens in sehr verdunnten wässrigen Lösungen," *Medd. K. Vetensk. Nobel Inst.*, **2**, Nr. 42 (1913); Faraday Lecture, *J. Chem. Soc.*, **105**, 1414 (1914).

[2] *J. Am. Chem. Soc.*, **40**, 106 (1918).

[3] *J. Am. Chem. Soc.*, **40**, 146 (1918).

[4] *Phil. Mag.*, **1**, 971 (1925); **4**, 233, 300 (1927); *Trans. Farad. Soc.*, **23**, 404 (1927).

curve which correspond with values of c chosen in any arbitrary geometrical progression of known ratio r. Let Λ and $\Lambda + \Delta\Lambda$ be values corresponding with c and rc; then from the Storch formula (p. 658):

$$\Lambda = \Lambda_0 - Bc^n,$$

$$\Lambda + \Delta\Lambda = \Lambda_0 - B(rc)^n,$$

$$\log(\Delta\Lambda) = n \log c - \log B(1 - r^n),$$

giving, since r is constant, a straight line, the slope of which gives n. From pairs of values of Λ, a series of values of Λ_0 may then be formed, the constancy of which affords a check on the validity of the equation over the range considered.

From Kohlrausch and Maltby's results for KCl the equation:

$$\Lambda = \Lambda_0 - 61.26c^{0.4520}$$

was found, and thence the following values of Λ_0:

$c \times 10^4$	1.0	2.0	5.0	10.0	20.0	50.0	100.0
Λ_0	130.02	130.07	130.08	130.04	130.00	130.00	130.07

These are in very good agreement. The method has been applied to 37 electrolytes and the formula holds from the lowest concentrations up to 0.01 N. The results have an important bearing on the validity of the Debye-Hückel equation, according to which $n = 0.5$. The following table shows that this

TABLE IX

FERGUSON AND VOGEL'S DATA FOR Λ_0

TEMP. 18° C.

Substance	Λ_0	B	n
KCl	130.04	61.26	0.4520
NaCl	109.02	54.24	0.4431
LiCl	99.07	51.74	0.4364
CsCl	133.07	80.97	0.5062
TlCl	131.04	152.73	0.5763
$MgCl_2$	111.63	83.87	0.3991
$LiClO_4$	88.33	103.32	0.6351
$BaBr_2$	126.8	100.9	0.3791
$CuSO_4$	114.16	810.2	0.5711
$Pb(NO_3)_2$	123.44	164.50	0.4520

is not generally true, and it is shown that the value of n is a linear function of the atomic weight in aqueous solutions of chlorides of the alkali metals. (See also, Fig. 10.)

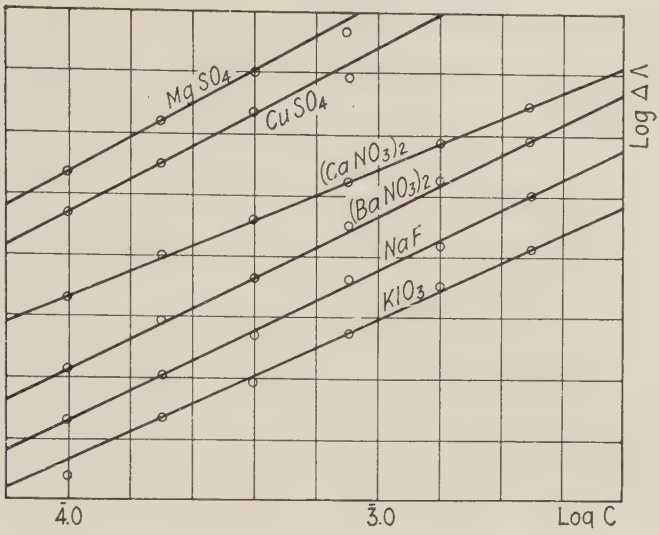

FIG. 10.

Debye and Hückel's Theory: An important theoretical conductivity formula was obtained by Debye and Hückel:[1]

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \left\{ \frac{\rho_2 r_1 + \rho_1 r_2}{\rho_1 + \rho_2} + \frac{\rho_1^2 + \rho_2^2}{2\rho_1\rho_2} \cdot \frac{e^2}{6DkT} \right\} \kappa$$

in which r_1, r_1 are the radii of the two ions of the salt;
ρ_1, ρ_2 are the frictional coefficients of the ions;
$1/\kappa$ is the thickness (radius) of the *ion atmosphere;*
D is the dielectric constant of the solvent;
k is Boltzmann's constant $= R/N$ (see p. 611);
T is the absolute temperature.

The equation can hold only in very dilute solutions.

On the assumption of Stokes' law (see pp. 15–19):

$$\rho = 6\pi\eta r.$$

Therefore,

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \left\{ \frac{2r_1 r_2}{r_1 + r_2} + \frac{r_1^2 + r_2^2}{2r_1 r_2} \cdot \frac{e^2}{6DkT} \right\} \kappa.$$

In deducing the equation the assumption is made that the electrolyte is *com-*

[1] *Physik. Z.*, **24**, 305 (1923); Müller, *ibid.*, **28**, 324 (1927); Gronwall, LaMer and Sandved, *ibid.*, **29**, 358 (1928); Debye, *Trans. Farad. Soc.*, **23**, 334 (1927); van Laar, *Z. anorg. Chem.*, **139**, 108 (1924).

pletely ionized and the variation of Λ with c is referred to changes in ionic mobilities. Each ion in solution is surrounded by an *ion atmosphere* containing, on the average, an excess of ions of opposite sign and characterized by the magnitudes $1/\kappa$, its *thickness*, and θ, the *relaxation time;* the values of $1/\kappa$ and θ are of the order of 10^{-8} cm./$\sqrt{c}$ and $10^{-10}/c$ secs., where c = conc. in mol/litre. θ defines the rate at which the ion atmosphere disappears if the central ion is supposed to be instantaneously removed.

The resistance offered to the motion of an ion depends on the viscous friction and also on two electrical effects: (i) the tendency of the applied field to displace the oppositely charged ion atmosphere, i.e., to displace the solvent (*electrophoresis*); (ii) the disturbance of the central symmetry of the ion atmosphere caused by the motion of the central ion, whereby a new ion atmosphere tends to build up around the displaced ion, and the old one left behind tends to disappear. These correspond with the "two new types of viscosity of electrical origin," postulated by Sutherland and Milner.[1] Both forces are inversely proportional to the thickness of the ion atmosphere, and since the latter is inversely proportional to $\sqrt{c}$ the formula:

$$\Lambda = \Lambda_0 - a\sqrt{c}$$

results. The theory stands or falls on the square-root law.

When the frequency of the applied alternating field is infinitely great compared with $1/\theta$, the dissymmetry of the ion atmosphere will not have time to develop, since the ion moves over about three times the thickness of the ion atmosphere in the relaxation time. The conductivity will then approach the value Λ_0, for infinite dilution, since the retarding effect due to the distortion of the ion atmosphere is absent. For intermediate values of the frequency, Λ will depend on the frequency, a so-called *dispersion effect*, which has been examined experimentally by Debye and Falkenhagen.[2]

If a very high field strength is applied, the ion will move too fast for its atmosphere to follow it, and again Λ will approach Λ_0 *at finite concentrations.* This effect has been observed by Wien,[3] who found deviations from Ohm's law for very high field strengths, giving rise to an increase of ionic mobility up to 56 per cent. Under these high applied voltages the ion would move over about 1 metre per sec. as compared with the usual speeds of about 0.01 mm. per sec.

Debye and Hückel's conductivity equation is:

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \sqrt{\frac{4\pi e^2}{DkT}} \cdot z \cdot c \left[\frac{e^2}{6DkT} w_1 + b w_2 \right]$$

where

[1] *Phil. Mag.*, **3**, 161 (1902); **9**, 781 (1905); **12**, 1 (1906); **14**, 1 (1907); **16**, 497 (1908); Milner, *ibid.*, **23**, 551 (1912); **25**, 742 (1913); **35**, 214 (1918); *Trans. Farad. Soc.*, **15**, 148 (1919).

[2] *Physik. Z.*, **29**, 124 (1928); *Z. Elektrochem.*, **34**, 562 (1928), Sack, *Physik. Z.*, **29**, 627 (1928); Falkenhagen and Williams, *Z. physik. Chem.*, **137**, 399 (1928).

[3] *Ann. Physik*, **73**, 161 (1924); **83**, 327 (1927); *Physik. Z.*, **28**, 834 (1927); Malsch and Wien, *Ann. Physik*, **83**, 305 (1927).

z_i = number of ions of the ith kind produced from one mol of salt,
$z = \sum z_i$,
c = concentration of salt in mols per c.c.,
e = electronic charge,
D = dielectric constant of solvent,
k = Boltzmann's constant,
T = absolute temperature.

$$w_1 = \frac{\sum z_i n_i^2 \rho_i}{\sqrt{z \sum z_i n_i^2}} \cdot \frac{\sum \frac{z_i n_i^4}{\rho_i^2}}{\sum \frac{z_i n_i^2}{\rho_i}}; \qquad w_2 = \sqrt{\frac{\sum z_i n_i^2}{z}}; \qquad b = \frac{\sum \frac{z_i n_i^2}{\rho_i} \cdot r_i}{\sum \frac{z_i n_i^2}{\rho_i}},$$

in which

n_i = valence of ith ion,
r_i = radius of ith ion,
ρ_i = frictional coefficient of ith ion = $6\pi\eta r_i$ if Stokes's law applies to the motion of the ions (see pp. 15–19).

For a uni-univalent electrolyte; $z_1 = z_2 = 1$; $n_1 = +1$; $n_2 = -1$.

$$\therefore \quad w_1 = \frac{1}{2} \frac{\rho_1^2 + \rho_2^2}{\rho_1 \rho_2}; \qquad w_2 = 1; \qquad b = \frac{r_1 \rho_2 + r_2 \rho_1}{\rho_1 + \rho_2}.$$

Now ρ is inversely proportional to the mobility of the ion, hence $\rho_1/\rho_2 = l_a/l_k$ and $\rho_2/\rho_1 = l_k/l_a$. Also if we substitute for ρ in b its value $6\pi\eta r$, we find $b = 2r_1 r_2/(r_1 + r_2)$, the harmonic mean of the ionic radii. By substituting w_1, w_2 and b in the above equation and simplifying we find

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \sqrt{2c}\left[\frac{K_1'}{(DT)^{3/2}} w + \frac{K_2'}{(DT)^{1/2}} b\right],$$

in which

$$K_1' = e^3\sqrt{\pi}/3k^{3/2}; \qquad K_2' = e\sqrt{\pi}/k^{1/2}$$

and

$$w = \tfrac{1}{2}(l_a/l_k + l_k/l_a).$$

If the equation is applied at a constant temperature we can also write:

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \left[\frac{K_1}{D^{3/2}} w + \frac{K_2}{D^{1/2}} b\right]\sqrt{2c}.$$

Onsager's Theory: The Debye-Hückel equation has been modified by Onsager [1] to take account of the Brownian movement of the central ion. He arrives at the formula for the mobility of an ion in $\text{ohm}^{-1}.\text{cm}^{-2}$.:

$$l_j = l_j^0 - \left(\frac{0.986.10^6}{(DT)^{3/2}} \cdot w l_j^0 + \frac{29.0\, z_j}{(DT)^{1/2}\eta}\right)\sqrt{(z_1 + z_2)c},$$

[1] *Physik. Z.*, **27**, 388 (1920); **28**, 277 (1927); *Trans. Farad. Soc.*, **23**, 341 (1927).

in which l_j^0 is the mobility at infinite dilution;

$$w = z_1 z_2 \cdot \frac{2q}{1 + \sqrt{q}},$$

$$q = \frac{z_1 z_2 (l_1^0 + l_2^0)}{(z_1 + z_2)(z_2 l_1^0 + z_1 l_2^0)};$$

c is the equivalent concentration; z_1, z_2 are the valences of the anion and kation; l_1^0, l_2^0 are the mobilities of anion and kation at infinite dilution; η is the viscosity. Thus, for the conductivity:

$$\Lambda = \Lambda_0 - \alpha\sqrt{\Gamma},$$

where Γ is twice the ionic strength $= (z_1 + z_2)c$;

$$\alpha = \frac{0.986.10^6}{(DT)^{3/2}} w\Lambda_0 + \frac{29.0}{(DT)^{1/2}\eta}(z_1 + z_2).$$

For water as solvent:

at 18° C. $\quad \alpha = 0.270 w\Lambda_0 + 17.85(z_1 + z_2)$

at 25° C. $\quad \alpha = 0.274 w\Lambda_0 + 21.14(z_1 + z_2)$

For binary electrolytes (valence of each ion = 2) the equation of Onsager becomes

$$l_j = l_j^0 - \left(\frac{5.78.10^5}{(DT)^{3/2}} z^2 l_j^0 + \frac{29.0\, z}{(DT)^{1/2}\eta} \right) \sqrt{2zc}.$$

The experimental curves show that Onsager's formulae are not very accurate at finite concentrations but they give roughly the correct slope of the curves at *infinite dilution*. An extension of the Debye and Hückel formula which gives good results at reasonable concentrations, is that proposed by Szyszkowski:[1]

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \frac{1}{2(\nu - 1)} [\beta c^{1/2} - 2\gamma c + 3\delta c^{3/2} + \cdots],$$

in which ν is the number of ions into which the salt ionizes, c is the concentration, and β, γ and δ are constants which are determined by trial.

The formula $\Lambda = \Lambda_0 - a\sqrt{c}$ does not give satisfactory results with some non-aqueous solutions[2] and the problem is still far from a satisfactory solution.

Nernst[3] has recently attempted to show that in addition to the Debye effect, there is also a *small* amount of unionized solute in a dilute solution of a strong electrolyte, obeying, with its ions, the law of mass action.

[1] *Bull. de l'Acad. Polonaise*, Series A, 1926, p. 325.

[2] Hartley and Bell, *Trans. Farad. Soc.*, **23**, 396 (1927); Ferguson and Vogel, *ibid.*, **23**, 405, 414 (1927); Hawkins and Partington, *ibid.*, **24**, 518 (1928).

[3] *Z. Elektrochem.*, **33**, 428 (1927); Orthmann, *Ergebn. d. exakt. Wiss.*, **6**, 155 (1927); Naude, *Z. Elektrochem.*, **33**, 532 (1927); Nernst, *Berl. Ber.*, **2**, 4 (1928); *Z. physik. Chem.*, **135**, 237 (1928); Nernst and Orthmann, *ibid.*, **135**, 199 (1928); Naude, *ibid.*, 209.

Conductance and Viscosity: The resistance offered to the motion of an ion in solution due to the viscosity may be expected to have some influence on conductance. This will be small below concentrations of about 0.1 *n.*, since such solutions usually have practically the same viscosity as pure water, but at higher concentrations the calculated ionization may be changed by 7 or 8 per cent according as viscosity is or is not taken into account. The effect of viscosity seems first to have been pointed out by G. Wiedemann in 1856.[1] and applied by Ostwald.[2]

At infinite dilution the separate ions should move independently, and it would be expected that the motion of the ions would then depend only on their nature and on the solvent. This does not appear to be accurately the case; [3] the product $\Lambda_\infty\eta$ (η = viscosity) varies somewhat from solvent to solvent, so that the equivalent conductance in one solvent cannot be calculated *accurately* from that in another by multiplication by the inverse ratio of the viscosities. If the conductivities of the individual ions are compared, the ratio varies from ion to ion, so that the ratios of Λ_∞ for the same solute in different solvents cannot be constant.

At moderately high concentrations the viscosity usually increases with the concentration, but sometimes in aqueous solutions it passes through a minimum. It depends both on solute and solvent. If the speeds of the ions depend on the viscosity, they will also depend on concentration, so that the equation of Kohlrausch-Arrhenius: $\alpha = \Lambda/\Lambda_\infty$, will no longer be true.

The work of Arrhenius [4] and of Lüdeking [5] seems to show that the ionic and bulk viscosities are not identical, because a jelly containing salt conducts almost as well after as before solidification. Arrhenius found that the temperature coefficient of *conductivity* of an electrolyte containing gelatin was practically the same as that of a solution free from gelatin, although the temperature coefficient of *viscosity* of gelatin solutions near the setting point is many times that of water. Lüdeking,[6] however, showed that

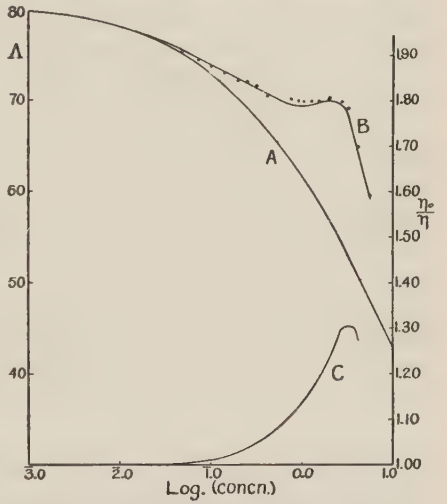

FIG. 11. Influence of viscosity change on conductivity of aqueous KCl soln. at 0°. A is the uncorrected curve, for Λ as determined, plotted from the equation $(c\Lambda)^2/c\Lambda_0(\Lambda_0 - \Lambda) = \text{const.}\ (c\Lambda/\Lambda_0)^{n-1}$, where const. = 2.62, $\Lambda_0 = 81.12$, $n = 1.51$ and B is the curve corrected for viscosity, i.e. $\Lambda' = \Lambda\eta/\eta_0$. C is the fluidity curve at 0°, i.e., the plot of η_0/η against log (concn.)

[1] *Ann. Physik*, **99**, 228 (1856).
[2] *Z. physik. Chem.*, **2**, 281 (1888).
[3] Kraus and Bray, *J. Am. Chem. Soc.*, **35**, 1383 (1913); Lattey, *Phil. Mag.*, **6**, 258 (1928).
[4] *Brit. Ass. Rep.*, p. 344 (1886).
[5] *Ann. Physik*, **37**, 172 (1889).
[6] Hatschek, The Viscosity of Liquids, 1928, p. 166; chap. 10 deals with the whole question.

this result is obtained only with low gelatin concentrations. Arrhenius[1] found that the conductivities in the presence of different non-electrolytes added so as to produce equal viscosities were not the same. The assumption of inverse proportionality between conductance and viscosity has often been made, i.e., that $(\Lambda/\Lambda_0)(\eta/\eta_0)$ gives a better value for α than the simple ratio Λ/Λ_0.[2] This simple proportionality between conductance and fluidity (1/viscosity) does not exist.[3] Green found that the relation $\Lambda = k\phi^m$, where ϕ = fluidity = $1/\eta$ and k and m are constants, holds, but the value of m varies with the electrolyte and with the added non-electrolyte. Johnson [4] considers that, except in the cases of $H^{\cdot}$ and OH' ions, the equivalent conductance of each ion is a function of fluidity, of the form $\Lambda = k\phi^m$, where m is a constant varying from 0.81 to 1.03 for various ions. This would lead to the expression: [5]

$$\alpha = \frac{\Lambda}{\Lambda_0}\left(\frac{\eta}{\eta_0}\right)^m = \frac{\Lambda}{\Lambda_0}\left(\frac{\phi_0}{\phi}\right)^m$$

for the ionization, η_0 being the viscosity of the pure solvent. The value of m is usually less than 1, but approaches 1 for slowly moving ions. The relation does not apply to acids and bases, for which the equation: $\alpha = \Lambda/\Lambda_\infty'$, is proposed,[6] in which Λ is the equivalent conductance of a solution above which the vapor pressure of water is p, and Λ_∞' is the value for infinite dilution when a non-electrolyte [7] is added so as to give the solution the same viscosity and vapor pressure as the first solution.

Change in viscosity may in general be brought about by: (i) change of concentration (including addition of a third substance), (ii) change of pressure, (iii) change of temperature. Kraus [8] has considered these factors separately in connection with ionic mobility. Solutions which exhibit a negative viscosity effect (i.e., viscosity *decreases* with concentration increase) have conductances directly proportional to the fluidity, and the same also probably holds for changes of viscosity due to change of external pressure. As a rule corrections cannot be made in this way with solutions exhibiting a positive viscosity effect (i.e., viscosity *increases* with concentration increase), although it may sometimes be applied by considering each ion separately. In the relation [6]

[1] *Z. physik. Chem.*, 9, 487 (1892).

[2] Bousfield and Lowry, *Phil. Trans.*, **204**, 289, 291 (1904); Noyes and Falk, *J. Am. Chem. Soc.*, **34**, 454 (1912).

[3] Green, *J. Chem. Soc.*, **93**, 2023, 2049 (1908); Sidgwick and Wilson, *ibid.*, **99**, 1118 (1911).

[4] *J. Am. Chem. Soc.*, **31**, 1010 (1909), cf. Philip and Oakley, *J. Chem. Soc.*, **125**, 1189 (1924); MacInnes, *J. Am. Chem. Soc.*, **43**, 1217 (1921)—application to separate ions; Hatschek, The Viscosity of Liquids, 1928, chap. 10.

[5] Washburn, *J. Am. Chem. Soc.*, **33**, 1461 (1911); Sachanov, *Z. Elektrochem.*, **19**, 588 (1913).

[6] Washburn and Williams, *J. Am. Chem. Soc.*, **35**, 750 (1913).

[7] The influence of non-electrolytes on ionization is discussed later.

[8] *J. Am. Chem. Soc.*, **36**, 35 (1914); see Fig. 11; cf. Rabinovitsch, *Z. physik. Chem.*, **99**, 338 (1921); Allmand, *Trans. Farad. Soc.*, **23**, 349 (1927); Onsager, *ibid.*, 356; Hatschek, Viscosity of Liquids, 119, 165, points out that the difficulty is to find a procedure for varying only one factor at a time.

$\Lambda/\Lambda' = \eta^m$, where Λ and Λ' are respectively the equivalent conductances in media of unit viscosity and viscosity η, the value of m approaches 1 with large ions and when the molecules of added non-electrolyte are small. This has been confirmed by Kieran[1] with solutions of HCl and KCl in presence of sucrose. It is considered that the change in the true transport number of an electrolyte with change of concentration is due to the different effects of viscosity on the two ions. In non-aqueous solutions, the ionic velocities change much less than the fluidities, although at high concentrations a marked influence is apparent. In such cases, correction of ionization for viscosity is not possible.

At higher temperatures, the velocities of the different ions in aqueous solutions tend to a common limit, which has been supposed to indicate that the ions become equal in size.[2] The equality in size has been assumed to indicate hydration, which would then increase with rise of temperature.[3]

The viscosity varies with pressure,[4] and the pressure effect also varies with temperature. In the case of pure water the viscosity decreases rapidly with increase in pressure, the rapidity of decrease being less as the temperature rises. At very high pressures the effect changes sign, and the viscosity increases with pressure (inferred from the shape of the curves). With non-aqueous solvents, viscosity increases with pressure,[5] the increase being greater the greater the viscosity. With increase of concentration the decrease in viscosity with pressure in the case of aqueous solutions becomes smaller and ultimately becomes an increase. The effect of pressure increases when the temperature is lowered.[6]

Influence of Non-Electrolytes: The conductance of aqueous solutions usually diminishes on addition of non-electrolytes in not too large amounts, the influence being exerted partly on the ionization and partly on the mobilities of the ions.[7] With further addition the conductivity slowly increases.[8] The

[1] *Trans. Farad. Soc.*, **18**, 119 (1922).

[2] Cf. Kohlrausch, *Ann. Physik*, **154**, 228 (1875); **62**, 209 (1897); *Sitz. ber. preuss. Akad.*, **26**, 572 (1902); Grotrian, *Ann. Physik*, **160**, 238 (1877); **8**, 259 (1879).

[3] Martin and Masson, *J. Chem. Soc.*, **79**, 707 (1901); Green, *ibid.*, **93**, 2023 (1908).

[4] Cohen, *Ann. Physik*, **45**, 666 (1892).

[5] Cohen, *loc. cit.;* Röntgen, *Ann. Physik*, **22**, 510 (1884); Warburg and Sachs, *ibid.*, **22**, 518 (1884).

[6] Cohen, *loc. cit.;* Schmidt, *Z. physik. Chem.*, **75**, 305 (1910). On viscosity effects in very concentrated solutions see Rabinowitsch, *Z. physik. Chem.*, **99**, 338, 417, 434 (1921). On viscosity and conductance see H. C. Jones and his co-workers, *Am. Chem. J.*, **37**, 405 (1907); **42**, 37 (1909); **46**, 131 (1911); *Z. physik. Chem.*, **61**, 641 (1908); **62**, 44 (1908); **81**, 68 (1912); **85**, 513 (1913); *J. Chim. Phys.*, **12**, 385 (1914); *J. Am. Chem. Soc.*, **37**, 1194 (1915).

[7] Stephan, *Ann. Physik*, **17**, 673 (1882); Lenz, *M. Acad. Petersb.*, **30**, No. 9 (1882); Arrhenius, *Z. physik. Chem.*, **9**, 487 (1892); Holland, *Ann. Physik*, **50**, 261 (1893); Strindberg, *Z. physik. Chem.*, **14**, 161 (1894); Walden, *ibid.*, **15**, 196 (1894); Cohen, *ibid.*, **25**, 1 (1898); Walker and Hambly, *J. Chem. Soc.*, **71**, 61 (1897); Roth, *Z. physik. Chem.*, **42**, 209 (1902); cf. Wildermann, *ibid.*, **46**, 43 (1903); Hartley, Thomas and Appleby, *J. Chem. Soc.*, **93**, 538 (1908); Green, *ibid.*, **93**, 2023, 2049 (1908).

[8] Arrhenius, *loc. cit.;* perhaps due to hydration of non-electrolyte.

effect is closely related to the viscosity change,[1] although colloids have usually only a slight effect,[2] except in large amounts.[3] The temperature coefficient of such solutions is usually nearly the same as that of pure aqueous solutions, unless the viscosity is greatly affected.[4]

Influence of Pressure on Conductivity: The influence of pressure on conductivity has been very thoroughly studied. The equation:

$$(d\ lnK/dp)_T = \Delta V/RT$$

was deduced by Planck[5] for dilute solutions. K is the equilibrium constant and ΔV the change of volume in the dissociation of 1 mol. of electrolyte. From this, the change in conductivity may be calculated. The effect has been examined experimentally [6] and the theory generally confirmed.

Körber, who used pressures up to 3000 kgm./cm.^{2}, found an increase of conductivity, the magnitude of the effect depending on temperature. In the case of acetic acid at 20° C. the results agreed with Planck's formula, but at higher temperatures the conductivity increased instead of decreasing according to the formula. The effects of pressure on ionic friction and viscosity of the solvent correspond in the case of sodium chloride but not for the potassium salt. The influence of pressure on ionic friction is additive for the two ions in the case of strong electrolytes. With increase of temperature the isothermals representing the influence of pressure on ionic friction for different electrolytes tend to approach one another, but $H^{\cdot}$ ions are exceptional. Up to the highest pressures the direction of the influence of pressure on the conductivity of strong electrolytes is independent of concentration up to moderate concentrations, but the magnitude of the effect becomes smaller as the concentration increases. For dilutions greater than 1 mol. in 100 liters, the effect of the solvent water becomes appreciable.

Schmidt examined the effect in non-aqueous solutions, using eleven organic solvents. The effect was divided into three factors: (i) change of volume, (ii) change of ionization, (iii) change of viscosity. The latter is not included in Planck's formula. The viscosity of water at low temperatures shows a

[1] Stephan, Arrhenius, *loc. cit.;* Massoulier, *Compt. rend.*, **130**, 733 (1900); *supra*, Viscosity.

[2] Levi, *Gaz. chim. ital.*, **30**, 64 (1900).

[3] E. Wiedemann, *Ann. Physik*, **20**, 537 (1883); Tietzen-Hennig, *ibid.*, **35**, 467 (1888); Lüdeking, *ibid.*, **37**, 172 (1889).

[4] Di Ciommo, *Nuov. Cim.*, **2**, 81 (1901); Starck, *Beibl. Ann. Physik*, **25**, 713 (1901). On conductivity of gelatine solutions see Palmer, Atchley and Loeb, *J. Gen. Physiol.*, **3**, 801 (1921).

[5] *Ann. Physik*, **32**, 494 (1887); Braun, *ibid.*, **30**, 250 (1887); *Z. physik. Chem.*, **1**, 259 (1887); see under Thermodynamics.

[6] Fink, *Ann. Physik*, **26**, 481 (1885); Fanjung, *Z. physik. Chem.*, **14**, 673 (1894); Piesch. *Ber. Wien Akad.*, **103**, 784 (1894); Lussana, *Nuov. Cim.*, **2**, 263 (1895); **5**, 357, 441 (1897); *Z. physik. Chem.*, **76**, 420 (1911); Tammann, *Z. physik. Chem.*, **17**, 725 (1895); Tammann and Bogojawlensky, *ibid.*, **27**, 457 (1898); Tammann, *Ann. Physik*, **69**, 767 (1899); Foussereau, *Compt. rend.*, **104**, 1161 (1887); Barus, *Am. J. Sci.*, **40**, 219 (1890); Körber, *Z. physik, Chem.*, **67**, 212 (1909); **77**, 420 (1911); Schmidt, *ibid.*, **75**, 305 (1910); Luther in Winkelmann's Physik, IV, i, 433 ff., for other factors supposed to influence conductivity.

minimum at a pressure of 1000 kgm./cm.^{2}, which disappears above 30°.[1] The relative importance of these was examined. The effect is much greater than in aqueous solutions in the case of strong electrolytes, but less in the case of weak electrolytes. The influence of pressure diminishes with rise of temperature and increase of concentration. In the case of NEt_4I the logarithm of the resistance increases proportionally to the pressure. With non-associating solvents the influence of pressure increases at 20° linearly with the viscosity of the solvent.

Drude and Nernst [2] pointed out that the experiments of Kohlrausch and Hallwachs [3] showed that the ionization of an electrolyte is always accompanied by a decrease in volume in the case of aqueous solutions, and they call this contraction of water in presence of free ions, *electrostriction.* It indicates that the dielectric constant of the solvent should be increased by pressure.[4] In aqueous solutions the contraction amounts to 10–12 cc. per equivalent of uni-univalent electrolyte ionized. In non-aqueous solutions [5] the corresponding figure is about 13 cc.

The relation

$$\Delta = \frac{\Lambda}{\Lambda_\infty}(A - B) + B,$$

where Δ is the percentage change in density per gram equivalent of dissolved electrolyte, and A, B are constants representing respectively the percentage changes in density caused by one gram equivalent of ionized and non-ionized electrolyte, has been put forward.[6] In the case of some electrolytes the values of B indicate that the dissolved electrolyte has the same volume as the solid salt, whilst salts forming hydrates in the solid state are hydrated in solution. Some electrolytes do not comply with the equation; the anomalies are traced to complex ions or the affinity of the salts for water. The density increase is greater the greater the sum of the mobilities of the constituent ions.

Von Hevesy [7] assumes that ions, or dispersed charged particles, tend to exhibit a constant potential difference between themselves and the solvent, amounting to about 70 millivolts. Ions with smaller radii will attach water molecules till this gives a radius of 2.8×10^{-8} cm. The solvent is contracted. If the size of the ion is increased beyond this by hydration, the mobility is reduced, since the P.D. is also reduced. Lorenz [8] has criticized the theory; it holds only for organic ions with 27 atoms. Those with fewer atoms have a

[1] Bridgman, *Proc. Nat. Acad.*, **11**, 462 (1925).

[2] *Z. physik. Chem.*, **15**, 79 (1894).

[3] *Ann. Physik*, **53**, 14 (1894); Kohlrausch, *ibid.*, **56**, 185 (1895).

[4] Non-electrolytes, see Polowzow, *Z. physik. Chem.*, **75**, 513 (1911).

[5] Carrara and Levi, *Gazetta*, **30**, ii, 197 (1900); Walden, *Z. physik. Chem.*, **60**, 87 (1907); Nernst, Lehrbuch, 8–11 Aufl., p. 449.

[6] Magie, *Phys. Rev.*, **25**, 171 (1909); Heydweiller, *Ann. Physik*, **30**, 873 (1909); *Z. anorg. Chem.*, **116**, 42 (1921) (tables of A and B); Clausen, *Ann. Physik*, **44**, 1067 (1914); **37**, 51 (1912), finds that with rise of temperature, A–B tends to the same value for all electrolytes.

[7] *Jahrb. Radioakt. Elektronik*, **2**, 419 (1914); **13**, 273 (1916).

[8] *Z. anorg. Chem.*, **105**, 175 (1919); cf. von Hevesy, *Kolloid Z.*, **21**, 129 (1917).

smaller, those with more a larger, radius than 2.8×10^{-8} cm. and there is no discontinuity in passing through this point.

Influence of Temperature on Conductivity: The specific conductance κ increases, usually, about 2 per cent per degree rise in temperature in aqueous solutions. Kohlrausch [1] represents the effect by the formula:

$$\kappa_t = \kappa_{18}[1 + \alpha(t - 18) + 0.0177(\alpha - 0.0177)(t - 18)^2],$$

where κ_t and κ_{18} are the conductivities at $t°$ C. and 18° C., and α is a specific constant which, in very dilute solutions, varies from 0.163 for HNO_3 to 0.0262 for Na_2CO_3.[2]

A more accurate form of Kohlrausch's equation is:[3]

$$\kappa_t = \kappa_{18}[1 + \alpha(t - 18) + 0.0163(\alpha - 0.0174)(t - 18)^2].$$

The equations may be applied to incompletely ionized electrolytes with close approximation.[4] Arrhenius pointed out that in such cases the heat of ioniza-

[1] *Sitz. ber. Preuss. Akad.*, 1026 (1901); 572 (1902).

[2] Temperature coefficients, see Kolrausch and Holborn, Leitvermögen, p. 146 ff.; Kohlrausch and Grotrian, *Ann. Physik*, **154**, 1, 215 (1875); Grotrian, **151**, 378 (1874); on fluidity, *ibid.*, **157**, 130 (1876); **160**, 238 (1877); **8**, 529 (1879); Kohlrausch, *ibid.*, **159**, 233 (1876); Otten, *Diss., Munich* (1887); Sack, *Ann. Physik*, **43**, 212 (1891); Holland, *ibid.*, **50**, 349 (1893); Beetz, *ibid.*, **117**, 1 (1862); Vincentini, *Atti Torino*, **20**, 869 (1885); Krannhals, *Z. physik. Chem.*, **5**, 250 (1890); Arrhenius, *ibid.*, **1**, 631 (1887); **4**, 96 (1889); **8**, 419 (1891); **9**, 339 (1892); Schaller, *ibid.*, **25**, 497 (1898); H. Jahn, *ibid.*, **16**, 72 (1895); Rudolphi, *ibid.*, **17**, 277 (1895); Dorn and Völlmer, *Ann. Physik*, **60**, 468 (1897); W. Foster, *Phys. Rev.*, **8**, 257 (1899); Kahlenberg, *J. Phys. Chem.*, **5**, 339 (1901); H. C. Jones and Douglas, *Am. Chem. J.*, **26**, 428 (1900); Lyle and Hosking, *Phil. Mag.*, **3**, 487 (1902); Hulett and Allen, *J. Am. Chem. Soc.*, **24**, 667 (1902); Hantzsch and Davidson, *Ber.*, **31**, 1612 (1898); Dennhardt, *Ann. Physik*, **67**, 325 (1899); A. A. Noyes, *Pub.* **63**, *Carnegie Inst. Washington*, 1907; Noyes and Coolidge, *Z. physik. Chem.*, **46**, 323 (1903) (NaCl and KCl to 306°); Kato, *Mem. Coll. Sci. Eng. Kyoto*, i, 332 (1908) (H_2SO_4 to 218°); Noyes and Falk, *J. Am. Chem. Soc.*, **34**, 454 (1912) (0° and 18°); Noyes and Johnston, *ibid.*, **31**, 987 (1909); Johnston, *ibid.*, **31**, 1010 (1909) (to 156°); Noyes, Kato and Sosman, *Z. Physik Chem.*, **73**, 1 (1910) (to 306°); Noyes, Melcher, Cooper and Eastman, *ibid.*, **70**, 335 (1909) (to 306°); Clausen, *Ann. Physik*, **37**, 51 (1911); H. C. Jones, *Pub.* **170**, *Carnegie Inst. Washington*, 1912 (0° to 65°); Jones and Getman, *Z. physik. Chem.*, **49**, 385 (1904); Jones and Jacobson, *ibid.*, **40**, 355 (1908); Jones and West, *Am. Chem. J.*, **34**, 357 (1905); **44**, 481 (1911); Jones and White, *ibid.*, **42**, 520 (1909); Jones and Howard, *ibid.*, **48**, 500 (1913); Jones and Winston, *ibid.*, **46**, 368 (1912); Bartoli, *Rend. Inst. Lombard.*, **28**, 246 (1895); Baur, *Z. physik. Chem.*, **23**, 409 (1897); Bousfield and Lowry, *Proc. Roy. Soc.*, **71**, 42 (1903); Déguisne, *Diss., Strasburg*, 1895; Euler, *Z. physik. Chem.*, **21**, 257 (1896); Felipe, *Physik. Z.*, **6**, 422 (1905); Gnesotto, *Atti Inst. Veneto*, **59**, ii, 987 (1900); Hechler, *Ann. Physik*, **15**, 157 (1904); Hunt, *J. Am. Chem. Soc.*, **33**, 795 (1911); Kunz, *Z. physik. Chem.*, **42**, 591 (1903); Lussana, *Atti Inst. Veneto*, **4**, 1466 (1893); Müller, *Bull. Soc. Chim. France*, **11**, 1001 (1912); Rasch and Hinrichson, *Z. Elektrochem.*, **14**, 46 (1908); Whetham, *Phil. Trans.*, **194**, 321 (1900); *Proc. Roy. Soc.*, **71**, 332 (1903); Wörmann, *Ann. Physik*, **29**, 194, 623 (1909); Wood, *Z. physik. Chem.*, **18**, 521 (1895); Normand, *J. Chem. Soc.*, **107**, 285 (1915); Rabinovitsch, *Z. physik. Chem.*, **99**, 338, 417, 434 (1921); Walden and Ulich, *ibid.*, **106**, 49 (1923); Wien, *Ann. Physik*, **77**, 560 (1925); Crowe, *Trans. Roy. Soc. Canada*, **21**, 145 (1927); for conductivity water, Parker and Parker, *J. Am. Chem. Soc.*, **46**, 312 (1924) give $\kappa_t = \kappa_o (1 + 0.0360t + 0.000215\, t^2)$.

[3] Luther, in Winkelmann's Physik, IV, i, 425.

[4] Arrhenius, *Z. physik. Chem.*, **4**, 96 (1889); **9**, 339 (1892); Euler, *ibid.*, **21**, 257 (1896); Rivals, *Compt. rend.*, **125**, 574 (1897); Steinwehr, *Z. physik. Chem.*, **38**, 185 (1901); Kortright,

tion is involved, and in some instances the decrease of ionization with rise of temperature may outweigh the increase of mobility, when a negative temperature coefficient results (e.g., phosphoric and phosphorous acids), and a maximum conductivity is reached at a particular temperature.[1] This is generally found also at high temperatures.[2] The temperature of the maximum is lower the more concentrated the solution. The work of Noyes and his collaborators showed that the higher the conductance of the solution the lower the temperature of the maximum and the lower the concentration at which the maximum appears at a given temperature. The more complex the salt the lower the temperature and the lower the concentration at which the maximum appears. For strong acids the maxima lie at temperatures considerably below those of binary salts. The ionization of strong electrolytes, apparently without exception, decreases with rise of temperature, but at lower temperatures the rate of decrease is relatively small. In the case of weak acids and bases the ionization increases between 0° and 40° and then decreases rapidly at higher temperatures. Sulphuric acid, which ionizes in stages, exhibits peculiarities at different concentrations. The ionization constant of water, $K_w = [H^\cdot][OH']$, increases very rapidly at lower temperatures, passing through a maximum about 218°, and then decreases:

	0°	18°	25°	100°	156°	218°	306°
$K_w \times 10^{14}$	0.089	0.46	0.82	48	223	461	168

The results with salts at high temperatures may be affected by hydrolysis.

Larmor [3] suggests that the temperature expression $1 + \alpha t + \beta t^2$ may be factorized: $(1 + at)(1 + bt)$, and considers that a expresses the effect on the viscosity of the solvent, and b that on the electrolyte. Lyle and Hosking [4] showed that the equivalent conductance and fluidity of solutions of NaCl, when plotted against temperature, give similar but not identical curves, which indicate that both Λ and fluidity would vanish at $-35.5°$ C. Rasch and Hinrichsen [5] suggest the relation $\log \kappa = -\gamma/T + C$, where γ and C are constants. Grotrian [6] had found that the temperature coefficients of fluidity and conductivity are approximately the same.

Wien [7] finds the relations

Am. Chem. J., **18**, 365 (1896); Hantzsch, *Ber.*, **32**, 3066 (1899); Guichard, *ibid.*, **32**, 1723 (1899); Abegg, *ibid.*, **33**, 393 (1900); Jaeger and Kapma, *Z. physik. Chem.*, **113**, 27 (1920) (accurate measurements to 1600° with fused salts).

[1] Cf. Sack, *Ann. Physik*, **43**, 212 (1891); Jones and MacKay, *Am. Chem. J.*, **19**, 83 (1897). Campbell, *J. Chem. Soc.*, 3021 (1926).

[2] Maltby, *Z. physik. Chem.*, **18**, 133 (1895); Hagenbach, *Ann. Physik*, **5**, 276 (1901); Kramers, *Arch. Néerl.*, **1**, 455 (1898); especially the work of Noyes and collaborators in preceding references.

[3] *Phil. Trans.*, **204**, 296 (1904).

[4] *Phil. Mag.*, **3**, 487 (1902).

[5] *Z. Elektrochem.*, **14**, 41 (1908); temperature effect with weak acids, see Mandala, *Gaz. chim. ital.*, **46**, 298 (1916).

[6] *Ann. Physik*, **157**, 130 (1875); **160**, 238 (1877).

[7] *Ann. Physik*, **77**, 560 (1925).

$$\alpha = \frac{1}{\phi} \cdot \frac{d\phi}{dt} = \frac{1}{a + bt}, \qquad \text{where} \qquad \phi = \text{fluidity};$$

$$\beta = \frac{1}{\kappa} \cdot \frac{d\kappa}{dt} = \alpha + \gamma, \qquad \text{where} \qquad \gamma \text{ is a constant.}$$

Except for Na_2CO_3 solutions, γ is negative; its values are: for salts -0.2 to -0.3; for bases -0.5 to -0.7; for acids -0.8 to -1.6. It is characteristic of each ion, and practically independent of concentration and temperature. The expression

$$\kappa_{t_2} = \kappa_{t_1}\{1 + q(t_2 - t_1)\}^p e^{\gamma(t_2 - t_1)}$$

where p, q are constants, is found on integration, in which the first factor depends on the viscosity and the exponential factor depends on the nature of the ion (see p. 666). This had been used as an empirical formula by Bousfield and Lowry; the negative sign of γ shows that the mobility of the ion does not increase with temperature so rapidly as the fluidity.

Kohlrausch's Law: A simple relation between values of Λ_∞ for various salts in dilute solution was discovered by F. Kohlrausch[1] in 1875, and confirmed by later more accurate measurements.[2] The following table gives values of Λ_∞ for two pairs of salts with common ions:

	K	Na
Cl	130.10	108.99
NO_3	126.50	105.33

The values ($KCl - KNO_3$) and ($NaCl - NaNO_3$) are 3.60 and 3.66, respectively; those of ($KCl - NaCl$) and ($KNO_3 - NaNO_3$) are 21.11 and 21.17, respectively. The difference for two kations is independent of the anions, and *vice versâ*. The relation, which is perfectly general in very dilute solutions, (including non-aqueous), shows (as Kohlrausch pointed out in 1875) that the limiting equivalent conductance of a salt is additively composed of two parts, the first depending only on the kation and the second only on the anion. This indicates that in solution the two ions move independently. Thus we can always write:

$$\Lambda_\infty = {}_\infty l_a + {}_\infty l_k.$$

The terms ${}_\infty l_a$ and ${}_\infty l_k$ are called by Kohlrausch the *mobilities* of anion and kation, respectively. The equivalent conductance at infinite dilution is the sum of the mobilities of anion and kation at a given temperature.

When values of Λ_∞ are known, the value of *one* mobility will enable all the rest to be calculated. The mobility is closely related to the Hittorf transport number, which gives the fraction of the total current carried by the ion, as will be explained later. Since the transport number of KCl is practically inde-

[1] *Göttinger Nachr.*, p. 213 (1876).

[2] Kohlrausch, *Ann. Physik*, **50**, 385 (1893); **66**, 785 (1898); *Sitzungsber. preuss. Akad. Wiss.*, 581 (1902); Leitvermögen, 1916, p. 104.

pendent of temperature and concentration, it was taken by Kohlrausch as the basis of his calculations. By a small extrapolation be found, at 18°,

$$_\infty l_k / _\infty l_a = 0.479/0.503.$$

Hence, $_\infty l_{K^\cdot} = 0.497 \times 130.10 = 64.6$, and $_\infty l_{Cl'} = 0.503 \times 130.10 = 65.5$. Thence, the values of the mobilities in the following table, referring to 18°, were calculated from the values of Λ_∞ for the salts. The table includes also the values of Noyes and Falk[1] whenever possible. Starred values are uncertain.

TABLE X

Mobilities of Ions in Aqueous Solutions at 18° C.

	l	$c \times 10^4$		l	$c \times 10^4$		l	$c \times 10^4$
$Li^\cdot$	33.3	265	SCN'	56.7	221	$\frac{1}{2}Mg^{\cdot\cdot}$	45.9	256
$Na^\cdot$	43.4	244	$C_5H_9O_2'$	25.7	244	$\frac{1}{2}Zn^{\cdot\cdot}$	47.0	254
F'	46.6	238	CHO_2'	47*	—	$\frac{1}{2}Cu^{\cdot\cdot}$	45.9	—
$Ag^\cdot$	54.0	229	$C_2H_3O_2'$	35*	238	$\frac{1}{2}Cd^{\cdot\cdot}$	46.4	245
$K^\cdot$	64.6	217	$C_3H_5O_2'$	31*	—	$\frac{1}{2}Sr^{\cdot\cdot}$	51.9	247
Cl'	65.5	216	IO_3'	34.0	234	$\frac{1}{2}Ca^{\cdot\cdot}$	51.9	247
$Tl^\cdot$	65.9	215	ClO_3'	55.1	215	$\frac{1}{2}Ba^{\cdot\cdot}$	55.4	239
I'	66.6	213	BrO_3'	47.6	—	$\frac{1}{2}Pb^{\cdot\cdot}$	60.8	240
Br'	67.7	215	IO_4'	48	—	$\frac{1}{2}Ra^{\cdot\cdot}$	58*	239
$Rb^\cdot$	67.5	214	ClO_4'	64	—	$\frac{1}{2}C_2O_4''$	63.0	231
$Cs^\cdot$	68	212	NO_3'	61.8	205	$\frac{1}{2}SO_4''$	68.5	227
$H^\cdot$	313.9[2]	154	OH'	174	180	$\frac{1}{2}CrO_4''$	72*	—
$NH_4^\cdot$	64.7	222	$\frac{1}{2}Ni^{\cdot\cdot}$	44	—	$\frac{1}{2}CO_3''$	60*	270
$\frac{1}{2}Be^{\cdot\cdot}$	28	—	$\frac{1}{2}Fe^{\cdot\cdot}$	45	—	$\frac{1}{4}Fe(CN)_6''''$	95.0	—
$\frac{1}{2}Mn^{\cdot\cdot}$	44	—	$\frac{1}{3}Fe^{\cdot\cdot\cdot}$	61	—	$\frac{1}{3}Al^{\cdot\cdot\cdot}$	40	—
$\frac{1}{2}Co^{\cdot\cdot}$	43	—	$\frac{1}{3}Cr^{\cdot\cdot\cdot}$	45	—	$\frac{1}{3}La^{\cdot\cdot\cdot}$	61.0	—
						$\frac{1}{3}Sm^{\cdot\cdot\cdot}$	53.5	—
						$\frac{1}{4}Th^{\cdot\cdot\cdot\cdot}$	23.5	—

The values of c are temperature coefficients, i.e., $(l_{t_2} - l_{t_1})/(t_2 - t_1)l$, where $l = (l_{t_1} + l_{t_2})/2$. From these the values at other temperatures than 18° may be calculated.

The physical meaning of Kohlrausch's law is clear from the point of view of the ionic theory: the conductivity is due only to the free ions, and is additively composed of the terms due to the latter. By addition of the values for $H^\cdot$ and $C_2H_3O_2'$, for example, we obtain the value of Λ_∞ for the weak acid CH_3COOH, which cannot be obtained directly. The values for the anions of weak acids and for the kations of weak bases may be found from the values of Λ_∞ for salts, since nearly all salts, even of weak acids and bases, are highly ionized at high dilutions. Thus, Λ_∞ for acetic acid = 313.9 + 35 = 348.9.

[1] *J. Am. Chem. Soc.*, **34**, 454 (1912).

[2] Kendall, *J. Chem. Soc.*, **101**, 1275 (1912).

The mass law

$$(\Lambda/\Lambda_0)^2 c/(1 - \Lambda/\Lambda_0) = \text{const.}$$

leads to the following equation for a weak electrolyte:

$$\Lambda_0 = \Lambda\Lambda_1(c\Lambda - c_1\Lambda_1)/(c\Lambda^2 - c\Lambda_1^2),$$

where Λ and Λ_1 are the equivalent conductances at concentrations c and c_1. Derick [1] points out that if the value so calculated for a weak acid such as acetic is in agreement with that calculated by subtracting ${}_0l_{Na^\cdot}$ from Λ_0 for the sodium salt, and adding to ${}_0l_{H^\cdot}$, the same value of Λ_0 should be found by the latter process as by the above method. This provides a check on the value of ${}_0l_{H^\cdot}$, and also serves to indicate whether a "water correction" is necessary in the case of organic acids and transition electrolytes.

The values of l for $H^\cdot$ and OH' are seen to be of great importance. They are noticeably higher than those for other ions, and their determination is difficult. Noyes and Sammet [2] give 329.8 at 18° for $H^\cdot$, and 174 for OH'. Kendall [3] gives for $H^\cdot$ the values 313.9 ± 0.4 at 18°, and 347.2 ± 0.4 at 25°. A large number of values for inorganic and organic ions are given by Bredig. These [4] require multiplication by 1.066 to reduce to ohm^{-1}. They refer to 25°.

When the solutions are not very dilute, Kohlrausch's law no longer holds. The deviations may be assumed due to incomplete ionization: [5]

$$\Lambda = \alpha({}_\infty l_a + {}_\infty l_k).$$

Hence,

$$\alpha = \Lambda/\Lambda_\infty.$$

The mobilities are here assumed constant, and since the conductance is proportional to the number of ions, the rate at which they move, and their charges, the changes of conductance are referred solely to changes in the number of ions. Another way is to assume the conductance always the sum of the mobilities, the latter varying with dilution:

$$\Lambda = l_a + l_l$$

This probably holds good at all concentrations, and gives the surest [6] form of Kohlrausch's theory.

Dissociation of Ternary Electrolytes: Kohlrausch [7] found that the limiting conductivity was reached at much higher dilutions in the case of salts such as $BaCl_2$ than in the case of KCl, and even higher dilutions in the case of salts

[1] *J. Am. Chem. Soc.*, **36**, 2268 (1914).

[2] *Z. physik. Chem.*, **43**, 49 (1903).

[3] *J. Chem. Soc.*, **101**, 1275 (1912), with discussion of previous values; Ulich, *Trans. Farad. Soc.*, **23**, 390 (1927) gives 351.5 at 25° C. for $H^\cdot$, and Hartley and Raikes, *ibid.*, 394, gives 349 at 25° C.

[4] *Z. physik. Chem.*, **13**, 191 (1894).

[5] Ostwald, *Z. physik. Chem.*, **2**, 840 (1888).

[6] Whetham, Theory of Solution, 1902, p. 226

[7] *Ann. Physik*, **26**, 161 (1885).

like $MgSO_4$. The calculation of the ionization is complicated when it occurs in stages:

$$AB_2 \rightleftharpoons AB^{\cdot} + B'; \qquad AB^{\cdot} \rightleftharpoons A^{\cdot\cdot} + B'$$

and it may be still further complicated by the presence of complex ions. Unless the extent to which each stage proceeds is known, the conductivity gives no indication of the state of ionization, owing to the different mobilities of the various ions. The matter has been considered by several investigators.[1] Jellinek (*loc. cit.*) points out that three different mobilities are in use; these are our l, u and U. The value of u depends on the valence (charge) of the ion; that of U is independent of valence. Lorenz (*loc. cit.*) shows that when an electrolyte dissociates without intermediate stages, the value of $\alpha = \mu/\mu_\infty$, μ being the *molar* conductance, gives correct results, whilst the ratio Λ/Λ_∞, Λ being the *equivalent* conductance, is equal to α only in the case of uni-univalent electrolytes.[2]

When intermediate ions are formed, however, μ/μ_∞ no longer gives the correct value of α. In such cases the ionization constants for the separate stages must be known.[3] Consider the case of a dibasic acid:

$$H_2A \rightleftharpoons H^{\cdot} + HA' \quad \therefore \quad k_1[H_2A] = [HA'][H^{\cdot}].$$
$$HA' \rightleftharpoons H^{\cdot} + A'' \quad \therefore \quad k_2[HA'] = [H^{\cdot}][A''].$$

$\therefore k_1k_2 = [H^{\cdot}]^2[A'']/[H_2A] = k_3$, the ionization constant for H_2A:

$$H_2A \rightleftharpoons 2H^{\cdot} + A''.$$

The value of k_1 may be found from measurements of the partition coefficient between solvents, when the concentration is such that the second stage of the ionization is inappreciable,[4] or from measurements of freezing-point, and thence

$$k_1 = \alpha^2/(1 - \alpha)V,$$

assuming the mass law, or from the conductivity $\alpha = \mu/\mu_\infty$, the value of μ_∞ being extrapolated by the Ostwald-Bredig rule. The mobility of HA' may also be found from conductivity measurements with the salt MHA, and by addition of $l_{H^{\cdot}}$ the value of μ_∞ for the acid HA' may be found.

[1] Steele, *Z. physik. Chem.*, **40**, 722 (1902); Kümmell, *Z. Elektrochem.*, **9**, 975 (1903); **11**, 94, 341 (1905); Noyes and Stewart, *J. Am. Chem. Soc.*, **32**, 1133 (1910); Göbel, *Z. physik Chem.*, **71**, 652 (1910); Deakin and Rivett, *J. Chem. Soc.*, **101**, 127 (1912); Wegscheider, *Sitz. Ber. Preuss. Akad. Wien*, ii, 441 (1902); Noyes and Falk, *J. Am. Chem. Soc.*, **34**, 485 (1912); McBain, *ibid.*, 1134; Drucker, etc., *Z. Elektrochem.*, **19**, 797 (1913); Wegscheider, *ibid.*, **20**, 18 (1914); Drucker, *ibid.*, **20**, 83 (1914); Wegscheider, *Monatsh.*, **23**, 599 (1902); **37**, 251 (1916); Lorenz, *Z. anorg. Chem.*, **95**, 340 (1916); **106**, 49, 63 (1919); Drucker, *Z. physik. Chem.*, **96**, 381 (1920); **38**, 602 (1901); Larsson, *Z. anorg. Chem.*, **125**, 281 (1922); **155**, 247 (1926); **172**, 375 (1928); McBain, *Z. Elektrochem.*, **11**, 215 (1905); Jellinek, *Z. physik. Chem.*, **76**, 257 (1911); Sherrill and Noyes, *J. Am. Chem. Soc.*, **48**, 1861 (1926); Prideaux and Ward, *J. Chem. Soc.*, **125**, 423 (1924); McCoy, *J. Am. Chem. Soc.*, **30**, 688 (1908); Chandler, *ibid.*, 694; Duboux, *J. Chim. phys.*, **19**, 179 (1921); Paul, *Z. physik. Chem.*, **110**, 417 (1924).

[2] Cf. Bousfield, *Trans. Farad. Soc.*, **15**, 74 (1919).

[3] Cf. Jellinek, *loc. cit.*; Harkins, *J. Am. Chem. Soc.*, **33**, 1838 (1911).

[4] Rothmund and Drucker, *Z. physik. Chem.*, **46**, 827 (1903); Drucker, *ibid.*, **49**, 563 (1904).

The value of k_2 may be found by measurement of $H^\cdot$ concentration in a solution of $MHA \rightleftharpoons M^\cdot + HA' \rightleftharpoons M^\cdot + H^\cdot + A''$ by an electrode, or by the conductivity of MHA at very high dilutions: $MHA \rightleftharpoons M^\cdot + HA' \rightleftharpoons M^\cdot + H^\cdot + A''$.[1] Let the total concentration of MHA be c and let the solution be so dilute that the MHA may be regarded as completely ionized and no M_2A molecules are present:

$$MHA = M^\cdot + HA'. \tag{1}$$

The HA' ions then undergo reaction in the following ways:

$$\begin{matrix} & HA' & = & H^\cdot & + & A''. \\ & c-x & & x & & x \end{matrix}$$

$$\begin{matrix} H^\cdot & + & HA' & = & H_2A. \\ y & & y & & y \end{matrix} \tag{3}$$

$$\begin{matrix} & 2HA' & = & H_2A & + & A''. \\ & 2\ z & & z & & z \end{matrix} \tag{4}$$

The concentrations are:

$$[A''] = x + z = y + z + [H^\cdot] \quad \text{since} \quad [H^\cdot] = x - y = [H_2A] + [H^\cdot], \tag{5}$$

$$[A''] + [HA'] + [H_2A] = x + z + (c - x - y - 2z) + y + z = c. \tag{6}$$

From (5) and (6) we find

$$[HA'] = c + [H^\cdot] - 2[A'']. \tag{7}$$

The law of mass action gives

$$[H^\cdot] \times [A''] = K_2[HA'], \tag{8}$$

hence

$$[HA'] = [H^\cdot] \times [A'']/K_2 = c + [H^\cdot] - 2[A'']$$
$$[H^\cdot] \times [A''] = K_2c + K_2[H^\cdot] - 2K_2[A''']. \tag{9}$$

Also, for the first stage of ionization:

$$[H^\cdot] \times [HA'] = K_1[H_2A],$$
$$[HA'] = K_1[H_2A]/[H^\cdot] = \frac{K_1[A''] - K_1[H^\cdot]}{[H^\cdot]}. \tag{10}$$

Substitute $[HA']$ from (8)

$$\frac{[H^\cdot] \times [A'']}{K_2} = \frac{(K_1[A''] - K_1[H^\cdot])}{[H^\cdot]},$$
$$[A''] = \frac{K_1K_2[H^\cdot]}{K_1K_2 - [H^\cdot]^2}. \tag{11}$$

[1] Braun, *Z. Elektrochem.*, **14**, 729 (1908); Luther, *ibid.*, **13**, 294 (1907); Göbel, *Z. physik. Chem.*, **71**, 657 (1910); Paul, *ibid.*, **110**, 417 (1924) gives eight methods for finding the second dissociation constant of a dibasic acid, k_2, with bibliography; Kraus, Electrically Conducting Systems, p. 105; Noyes, *Z. physik. Chem.*, **11**, 495 (1893); Smith, *ibid.*, **25**, 193 (1898)—data.

Substitute in (9) and simplify; then

$$K_2 = \frac{(K_1 + c + [H^\cdot])[H^\cdot]^2}{K_1(c - [H^\cdot])} = \frac{(K_1 + c)[H^\cdot]^2}{K_1 c} \quad \text{approximately.} \quad (12)$$

Since c and K_1 are known, a measurement of $[H^\cdot]$ in the solution gives K_2.

The value of K_2 may also be found by measurements of the conductance of the acid at high dilutions, when the first stage of the ionization:

$$H_2A = H + HA'$$

may be regarded as complete. Then, for 1 mol in V litres:

$$\begin{matrix} HA' & = & H^\cdot & + & A'' \\ 1 - a & & a & & a \end{matrix}$$

$[H^\cdot] = 1 + a$ and hence

$$K_2 = \frac{[H^\cdot] \times [A'']}{[HA']} = \frac{a(1 + a)}{V(1 - a)}. \quad (13)$$

If the mobilities of the ions HA' and A'' are known (say from the conductivities of salts MHA and M_2A) then the molar conductance of the acid at the dilutions considered will be

$$\mu = l_{HA'}(1 - a) + l_{H^\cdot}(1 + a) + a l_{A''};$$

$$\therefore \quad a = \frac{\mu - l_{HA'} - l_{H^\cdot}}{l_{H^\cdot} + l_{A''} - l_{HA'}}, \quad (14)$$

from which K_2 may be calculated by the formula (13).

Absolute Mobilities: From the values of l_a and l_k expressed in ohm^{-1} it is possible to calculate the absolute velocities in cm. per sec. under a potential gradient of 1 volt per cm., represented by v and u, or under a force of 1 dyne, represented by V, U.[1] Consider the solution in a centimeter cube with electrodes at opposite faces, and let there be a P.D. of 1 volt between the electrodes (Fig. 12). The current through the cell will be the specific conductance, κ ampère. Let the concentration η be so small that the solute is completely ionized, then the number of coulombs transported per second is:

Fig. 12

$$\kappa = \eta\Lambda_\infty = \eta({}_\infty l_a + {}_\infty l_k).$$

All kations in a length u of the cube will have moved through a given section in 1 second, and similarly all the anions in a length v. These are $u\eta$ gm. equiv. and $v\eta$ gm. equiv., respectively. Each equivalent transports $F = 96{,}500$ coulombs, hence the transport in both directions per second will be $96{,}500(u + v)\eta$. This is the total current, hence:

$$\eta({}_\infty l_k + {}_\infty l_a) = 96{,}500\eta(u + v);$$

$\therefore u = 0.0_41036\ {}_\infty l_k$ and $v = 0.0_41036\ {}_\infty l_a$ in cm./sec. per volt/cm.

[1] Kohlrausch, *Ann. Physik*, 6, 196 (1879); Leitvermögen, p. 105; Budde, *Ann. Physik*, 156, 618 (1875).

To find U and V we remember that 1 electromagnetic unit of quantity is 10 coulombs, and that 1 volt is 10^8 E.M.U. The force acting on 1 gm. equiv. is 9650×10^8 dynes. The force and velocity are proportional, on account of the viscous drag, hence the forces required to impart unit velocity to each ion are $9650 \times 10^8/u$ and $9650 \times 10^8/v$, respectively. The velocities under unit force (1 dyne) are thus:

$$U = u/9650 \times 10^8 \text{ cm./sec.}, \qquad \text{and} \qquad V = v/9650.10^8 \text{ cm./sec.}$$

Since 1 gram weight is 981 dynes, the forces in kgm. wt. to impart unit velocity are $9.8 \times 10^5/u$ and $9.8 \times 10^5/v$. If M is the equivalent weight, the forces per gram of ion are $9.8 \times 10^5/M_1u$ and $9.8 \times 10^5/M_2v$. To impart unit velocity to 1 gram of potassium ions requires a force of 38,000,000 kgm. wt. This explains the extreme slowness of motion of ions in solution. From the values of l_k and l_a the velocities of $K^{\cdot}$ and Cl' ions under a potential gradient of 1 volt/cm. are calculated from the above equations as 0.00066 cm./sec., and 0.00067 cm./sec., respectively.

The force required to impart unit velocity to a single ion is $9.8.10^5/N_0u$ kgm. wt., where N_0 = Avogadro's constant. For the $K^{\cdot}$ ion this is 2.5×10^{-9} milligram weight.

The general equation for conductivity is:

$$\kappa = \sum n_+q_+u + \sum n_-q_-v,$$

where n = no. of mols of ion per cc., q = charge on ion

$$\therefore \quad \kappa = \sum n_+\nu_+\mathbf{F}u + \sum n_-\nu_-\mathbf{F}v,$$

where ν = valence of ion. This holds for mixtures of salts.

The Migration of Ions: Transport Number. Indications that ions move at unequal rates in electrolysis had been obtained by Gmelin,[1] and especially by Daniell and Miller,[2] but on account of the great experimental difficulties no reliable information was available until the work of Hittorf,[3] begun in 1853.

The principle of the method is seen from Fig. 13. The trough AB is divided by partitions C and D, either real (apparatus with diaphragms) or imaginary (apparatus without diaphragms), into three parts. These diaphragms are perfectly permeable and their object is to prevent mixing of the liquids by diffusion. Let the trough be filled with an electrolyte, say HCl, the ions of which move with speeds in the ratio $H^{\cdot}/Cl' = 5/1$. Let 1 F be passed through from electrodes A and B. The following changes occur:

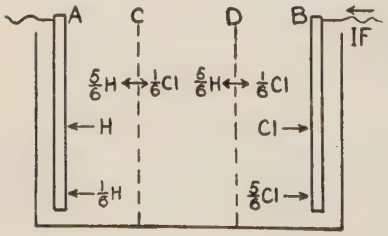

FIG. 13

[1] *Ann. Physik*, **44**, 30 (1838).

[2] *Phil. Trans.*, **134**, 1 (1844).

[3] *Ann. Physik*, **89**, 177 (1853); **98**, 1 (1856); **103**, 1 (1858); **106**, 337, 513 (1859); reprinted in Ostwald's *Klassiker*, Nos. 21 and 23, *Leipzig*, 1891; *Ann. Physik*, **4**, 374 (1878); *Z. physik. Chem.*, **39**, 613 (1901); **43**, 239 (1903); Hittorf and Salkowski, *ibid.*, **28**, 546 (1899).

(i) *In AC.* Total loss of $H^{\cdot} = 1$ equivalent, of which 5/6 migrated in from *CD* and hence 1/6 was taken from *AC*. Also 1/6 Cl′ has migrated from *AC* to *CD*. Thus 1/6 mol. HCl is lost from *AC*.

(ii) *In CD.* There is a migration of 5/6 $H^{\cdot}$ from *BD* and 5/6 $H^{\cdot}$ to *AC*. Also 1/6 Cl′ migrates in from *AC* and 1/6 Cl′ out to *BD*. Total loss nil.

(iii) *In BD.* Total loss of Cl′ is 1 equivalent, of which 1/6 migrates in from *CD* and 5/6 therefore come from *BD*. Also 5/6 $H^{\cdot}$ migrate out of *BD* to *CD*. The total loss of HCl from *BD* is 5/6 mol.

The losses in *neutral electrolyte molecules* (HCl) round the electrodes are in the ratio of the velocities of the ions moving away from the electrodes. This result is easily generalized.[1]

If in electrolysis 1 equivalent of kation is deposited, a fraction n is taken from the immediate vicinity of the electrode, and the fraction $(1 - n)$ migrates into the kathode space from the bulk of the solution. Thus n equivalents of anion must migrate out of the kathode space to make up the total charge F crossing any section of the electrolyte. The current is carried by anions and kations in the ratio $n : (1 - n)$. The fraction n was called by Hittorf the *transport number* of the anion. The transport number of the kation is $1 - n$.

If l_k, l_a are the mobilities of the two ions, then, by definition:

$$l_k/l_a = (1 - n)/n.$$

This gives the ratio of l_k/l_a when n is known; their sum is equal to Λ, hence l_k and l_a may be calculated separately.[2] The general equation for transport number is:

$$n_1 = \frac{n_1 q_1 v_1}{\sum n_+ q_+ u + \sum n_- q_- v}$$

with the condition

$$\sum n_+ q_+ = \sum n_- q_-.$$

Lorenz[3] points out that the assumption of complete ionization (p. 661) requires a new definition of transport number, viz.,

$$n = xu_0/(xu_0 + yv_0),$$

where x and y are separate mobility coefficients for kation and anion. Kohlrausch's formula $\Lambda = \alpha F(u + v)$ is then replaced by $\Lambda = F(xu_0 + yv_0)$, where u_0 and v_0 are limiting values approached at infinite dilution. The rate of change of mobility with concentration is different for different ions.

[1] See Larmor, Æther and Matter, Cambridge, 1900, p. 290.

[2] F. Kohlrausch, *Götting. Nachr.*, 1876, p. 213; cf. pp. 539, 540.

[3] *Z. anorg. Chem.*, **111**, 55 (1920); Lorenz and Landé, *ibid.*, **125**, 59 (1922); Lewis, *J. Am. Chem. Soc.*, **34**, 163 (1912) suggested that the ion mobilities in nearly all cases change with concentration, and that the change of Λ with dilution, in the case of strong electrolytes, is largely due to this variation. This was also the principal feature of Sutherland's theory. *Phil. Mag.*, **3**, 161 (1902); **9**, 781 (1905); **12**, 1 (1906); **14**, 1 (1907); **16**, 497 (1908); cf. Barmwater, *Z. physik. Chem.*, **28**, 115 (1899).

There is never the slightest separation of the ions in the bulk of the solution, and the result is independent of the ultimate fate of the ions which move.[1]

In the case of mixed electrolytes, Hittorf assumed that they carry the current in the ratio of their conductivities. The detailed calculation, which involves the theory of ionization, shows that the quantity of any ion passing a cross section is proportional to its concentration in the mixture and to its mobility. In the case of a mixture of KCl and NaCl, say, of total concentration c, and with the ratio $[KCl]/[NaCl] = x$:

$$n_K = \frac{xcl_K}{c(xl_K + (1 - x)l_{Na} + l_{Cl}} \tag{1}$$

on the assumption that each salt is equally ionized and that no complexes are formed, the mobility being constant at any given *total* salt concentration. For $x = 1$. This gives $\overline{n}_K = l_K/\Lambda_{KCl}$, and for the pure salts

$$(1 - \overline{n}_K)\Lambda_{KCl} = (1 - \overline{n}_{Na})/\Lambda_{NaCl};$$

$$\therefore \quad \overline{n}_K = n_K(1 - n_{Na})/[(n_K - n_{Na}) + (1 - n_K)/x].$$

The numerator in (1) is the current carried by the K ions only; the denominator is the total current carried by all ions.[2]

Determination of Transport Numbers: In the determination of transport numbers the possibility of the existence of complex ions must be kept in mind, and, if these are present, the transport of one ion only will not give correct results. In some cases the metal ion may unite with salt, or a complex anion may be formed, by which metal is carried to the anode. The presence of complex ions may be detected by transport measurements.[3]

[1] Hittorf, *Ann. Physik*, **103**, 1 (1858). See also Whetham, *Phil. Trans.*, **184**, 337 (1893); *Z. physik. Chem.*, **11**, 220 (1893); Kohlrausch, *Ann. Physik*, **62**, 209 (1897); Weber, *Z. physik. Chem.*, **4**, 182 (1889); *Sitz. ber. preuss. Akad.*, p. 567 (1897); Masson, *Phil. Trans.*, **192**, 331 (1899); *Z. physik. Chem.*, **29**, 501 (1899); Steele, *ibid.*, **40**, 689 (1902); Abegg and Gauss, *ibid.*, **40**, 737 (1902); Kümmel, *Ann. Physik*, **46**, 105 (1892); Zahn, *ibid.*, **48**, 606 (1893); Lorenz and Posen, *Z. anorg. Chem.*, **95**, 340 (1916).

[2] Stackelberg, *Z. physik. Chem.*, **23**, 493 (1897); Hopfgartner, *ibid.*, **25**, 115 (1898); Hoffmeister, *ibid.*, **27**, 345 (1898); Schrader, *Z. Elektrochem.*, **3**, 498 (1897); Rieger, *ibid.*, **7**, 863 (1901); Pfanhauser, *ibid.*, **7**, 698 (1901); Hellwig, *Z. anorg. Chem.*, **25**, 157 (1901); McGregor and Archibald, *Phil. Mag.*, **45**, 151 (1898); Braley and Hall, *J. Am. Chem. Soc.*, **42**, 1770 (1920); Schneider and Braley, *ibid.*, **45**, 1121 (1923); Stearne, *ibid.*, **44**, 670 (1922); MacInnes, *ibid.*, **47**, 1922 (1925); Dewey, *ibid.*, p. 1927; Ruby and Kawai, *ibid.*, **48**, 1119 (1926); Braley and Rippie, *ibid.*, **48**, 1493 (1926).

[3] Hittorf, *Ann. Physik*, **106**, 513 (1859); Rosenheim, *Z. anorg. Chem.*, **11**, 175 (1896); Kistiakowski, *Z. physik. Chem.*, **6**, 97 (1890); Hellwig, *Z. anorg. Chem.*, **25**, 157 (1901); Morse, *Z. physik. Chem.*, **41**, 709 (1902); Kremann, *Z. anorg. Chem.*, **33**, 87 (1903); **35**, 48 (1903); Bredig, *ibid.*, **34**, 202 (1903); Coehn, *Ber.*, **35**, 2673 (1902); Whetham, *Phil. Trans.*, **184**, 358 (1893); Steele, *ibid.*, **198**, 133 (1902); Schlundt, *J. Phys. Chem.*, **6**, 159 (1902); Heym, *Ann. Physique*, **12**, 443 (1919); Falk, *J. Am. Chem. Soc.*, **32**, 1555 (1910); Braley and Hall, *ibid.*, **42**, 177 (1920); Hixon, *Medd. K. Vetensk. Nobel Inst.*, **4**, No. 12 (1922); Schneider and Braley, *J. Am. Chem. Soc.*, **45**, 1121 (1923); Bray and Mackay, *ibid.*, **32**, 914 (1910); Sandonnini, *Gazetta*, **46**, ii, 205 (1916); Lorenz and Posen, *Z. anorg. Chem.*,

The principal types of apparatus used are shown in Fig. 14. Type *a*, used by Hittorf, is provided with membranes; the anode, usually cadmium, is in the lower vessel, and the platinum kathode in the upper. The membranes are not without influence on the results,[1] and are not now used. Apparatus *b*, used by Hittorf, Lenz,[2] Hopfgartner,[3] Jahn [4] and Rieger,[5] is provided with a glass plug for separating the anode and kathode spaces after the experiment,

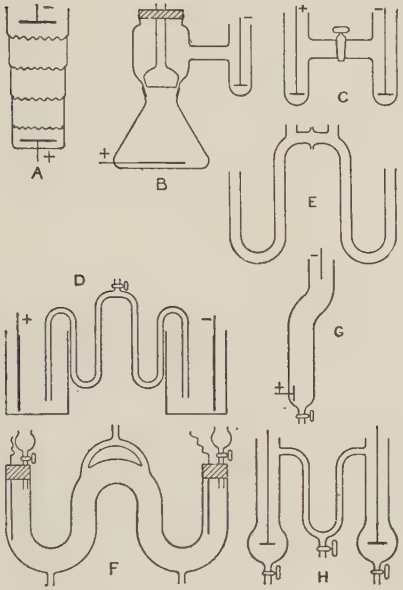

Fig. 14. Types of Transport Number Apparatus

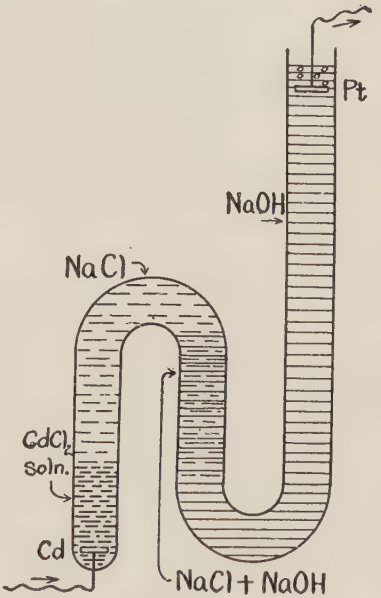

Fig. 15. Hittorf's Transport Number Apparatus

and is a good type. Type *c* is a simple one used by Weiske,[6] Lussana,[7] Hellwig, Rieger, and Mather,[8] in which the spaces are separated by a wide stopcock. In type *d*, used by Wiedemann [9] and Kirmis,[10] the separation is effected by

95, 340 (1916); Drucker, *Z. Elektrochem.*, **18**, 236 (1912); Costachescu and Apostoi, *Ann. Sci. Univ. Jassy*, **7**, 101 (1912); Hamer and Bury, *J. Chem. Soc.*, 1927, p. 333; Jaques, Complex Ions, 1914, Chap. III.

[1] Bein. *Z. physik. Chem.*, **28**, 439 (1898); Hittorf, *ibid.*, **39**, 613 (1901); **43**, 239 (1903).

[2] *Ann. Physik Beibl.*, **7**, 399 (1883).

[3] *Z. physik. Chem.*, **25**, 119 (1898); Schilow, *Z. anorg. Chem.*, **133**, 55 (1924).

[4] *Z. physik. Chem.*, **37**, 673 (1901); **38**, 127 (1902).

[5] *Z. Elektrochem.*, **7**, 863 (1901).

[6] *Ann. Physik*, **103**, 466 (1858).

[7] *Atti. Inst. Veneto*, **3**, 1111 (1892); **4**, 1563 (1893).

[8] *Am. Chem. J.*, **26**, 473 (1901).

[9] *Ann. Physik*, **87**, 321 (1852); **99**, 177 (1856).

[10] *Ann. Physik*, **4**, 503 (1878).

letting air into the siphon. Type *e* was used by Noyes.[1] After electrolysis the ends are closed and liquid pipetted from the upper tubulures. During electrolysis Noyes kept the liquids round the electrodes constantly neutral by adding acid or alkali. In types *f*, *g*, and *h*, used by Nernst and Loeb (type *g* modified),[2] Bein (type *h* modified),[3] Kistiakowski (type *g*)[4], Carrara (type *h*) [5] and Denison and Steele (type *f*),[6] the liquids may be run out and weighed. Type *h* is a good one. The object of the bulbs is to decrease resistance, which causes heating and convection currents.

Hittorf[7] used the apparatus shown in Fig. 15. Cadmium is used for the anode, platinum for the kathode. The electrolyte is NaCl. $CdCl_2$ is formed at the anode, and $Cd^{\cdot\cdot}$ ions move towards the kathode, but, being slow, never catch the $Na^{\cdot}$ ions, the two layers of liquid remaining separate as shown. At the kathode, all the Cl' ions have migrated away and are replaced by OH' ions from the water, and, as these are fast ions, there is mixing, as shown. The hydrogen rises from the kathode and does not cause mixing in the bulk of the liquid.

The original NaCl solution contained 0.01784 per cent Cl and was contained in an apparatus in three parts, with taps. The weights of solution in these were: anode part, 226.99 gm.; middle part, 195.24 gm.; kathode part, 331.49 gm. The weights of Cl in these before electrolysis were therefore 0.04048 gm., 0.03482 gm., and 0.05913 gm. (Note the small quantities.) The weights found after the experiment were 0.04671 gm., 0.03483 gm., and 0.05289 gm. The middle part was unchanged, the anode gained 0.00623 gm., and the kathode lost 0.00624 gm. A voltage of 150 was applied for 108 minutes, and the weight of silver deposited in a coulometer in series was equivalent to 0.01021 gm. Cl. (Note the small weights involved.) The migration ratio of Cl in NaCl is thus $0.00624/0.01021 = 0.611$. This example has been given to show the weak currents, long times, and small transports which must be used in such experiments. In Noyes' experiments, on the other hand, a current of 0.02 to 0.18 amp. was used for 7 hours, a much greater transport was obtained, and the results were correspondingly more accurate.

The following table gives some directly measured transport numbers of the anions of salts. Values marked * are less accurate. The temperature is 18° and aqueous solutions were used. The concentrations are in gm. equivalents per *liter*.[8]

In the case of uni-univalent salts the ratio is not very dependent on con-

[1] *Z. physik. Chem.*, **36**, 63 (1901).
[2] *Z. physik. Chem.*, **2**, 948 (1888).
[3] *Ibid.*, **27**, 23 (1898).
[4] *Ibid.*, **6**, 105 (1890).
[5] *Mem. Acad. Lincei*, **4**, 338 (1901).
[6] *J. Chem. Soc.*, **81**, 456 (1902).
[7] Cf. *Ann. Physik*, **103**, 1 (1858); also Bein, *loc. cit.*
[8] Kohlrausch and Holborn, Leitvermögen, pp. 213 ff.; Luther, Winkelmann's Physik, IV, i, 889 ff.; Baars in Geiger and Scheel's Handbuch der Physik, **13**, 425 (1928).

TABLE XI

TRANSPORT NUMBERS OF ANIONS OF SALTS IN AQUEOUS SOLUTIONS AT 18° C.

$m =$	0.005	0.01	0.02	0.05	0.1	0.2	0.5	1	2	5
KCl	.504	.504	.504	.505	.506	.506	.510	.515	.515	.516*
NH_4Cl	.507	.507	.508	.508	.509	.510	.513	.514	.515	.516*
KI	—	.506	.507	.507	.508	.509	.513	.514	.515	.516*
NaCl	.603	.604	.604	.605	.607	.610	.623	.637	.642*	.650*
LiCl	.670	.670	.672	.680	.687	.696	.73	.74	.745	.774*
KNO_3	—	—	—	—	.497	.496	.492	.487	.479	—
$AgNO_3$	.526	.526	.526	.526	.526	.522	.51	.50	.476	—
KOH	—	—	—	—	.735	.736	.738*	.740*	—	—
HCl	.168	.167	.166	.165	.164	.163	.155	.155	.18*	.24*
$\frac{1}{2}BaCl_2$	—	.56*	.565*	.575*	.585*	.595*	.615*	.640*	.657	—
$\frac{1}{2}CdI_2$	.555	.556	.557	.604	.704	.873	1.003	1.12	1.22	2.5
$\frac{1}{2}CuSO_4$	—	—	.625	.625	.627	.640	.67	.696	.72	—

centration to about 0.2 $n.$, indicating a practically constant ratio of l_a and l_k.[1] Sodium salts are less constant than potassium salts. Silver nitrate, which has been very carefully investigated, also shows constant results. Acids and bases with univalent ions give constant ratios up to about 0.2 n.[2] Other salts show deviations even at 0.01 n. Cadmium iodide exhibits a strong tendency to complex ion formation, giving a value of n ultimately greater than unity. Sulphates give less constant values than halogen salts, indicating greater tendency to complex formation.[3]

The Moving Boundary Method: Lodge [4] filled a tube with saline jelly, to which phenolphthalein was added, colored red by a trace of alkali. One end was in contact with dilute acid, and on passing a current the color was progressively bleached, and from the rate of motion of the boundary the velocity of $H^{\cdot}$ was found to be 0.0025 cm. sec. per volt/cm., as compared with 0.0032 from Kohlrausch's method and the transport number. Another method in which copper ions were driven through a solution just so fast that they were able to carry the current without deposition of hydrogen was used by C. L. Weber.[5]

[1] Kohlrausch, *Ann. Physik.*, **50**, 388 (1893); Jahn, *Z. physik. Chem.*, **27**, 354 (1898), **33**, 545 (1900); **35**, 8 (1900); **37**, 673 (1901); **58**, 641 (1907); Noyes and Kato, Carnegie Inst. Washington Publ., No. **63**, 326 (1901); Sutherland, *Phil. Mag.*, **3**, 161 (1902); **9**, 781 (1905); **12**, 1 (1906); **14**, 1 (1907); **16**, 497 (1908); Drucker and Krsnjavi, *Z. physik. Chem.*, **62**, 731 (1908); Sackur, *Z. Elektrochem.*, **7**, 786 (1901); Goodwin and Haskell, *Z. physik. Chem.*, **52**. 630 (1905); Loeb and Nernst, *ibid.*, **2**, 956 (1888); Bein, *ibid.*, **27**, 41 (1898); Noyes, Technological Quarterly, **17**, 295 (1904); Arrhenius, *Z. physik. Chem.*, **37**, 315 (1901); Abegg, *Ahrens' Sammlung*, Theorie der elektrolytischen Dissociation, 1903, p. 232; G. N. Lewis, *J. Am. Chem. Soc.*, **34**, 1631 (1912) are some of the earlier memoirs dealing with the effect of concentration on n. See p. 661 on the Debye-Hückel theory.

[2] Kraus, Electrically Conducting Systems, p. 26, thinks variations at higher concentrations are connected with changes of viscosity.

[3] Kümmel, *Ann. Physik*, **64**. 655 (1898).

[4] *Brit. Ass. Rep.*, 1886, p. 389.

[5] *Z. physik. Chem.*, **4**, 182 (1889); Sheldon and Downing, *Phys. Rev.*, **1**, 51 (1893).

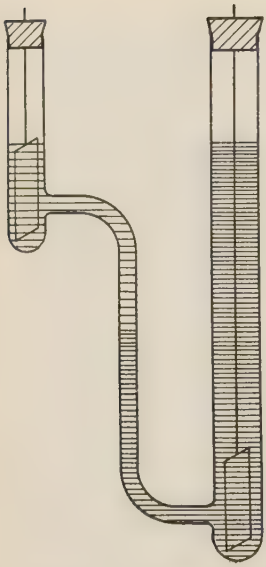

Fig. 16. Whetham's Apparatus for Moving Boundary Measurements

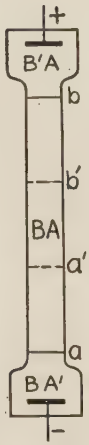

Fig. 17

Lodge's method was improved by Whetham,[1] who used two solutions with a common ion, with the same concentrations and nearly the same specific conductances, but different in color and density, stratified in a vertical tube (Fig. 16). In one case 0.1 n. $K_2Cr_2O_7$ and K_2CO_3 were used. The colored ion moved and the rate of motion of the boundary could be followed. Addition of agar did not affect the results, and the Lodge method could be used. The gradient of potential was constant through the tube, and from the measured current and the motion of the boundary the mobilities could be calculated. They agreed with Kohlrausch's values.

The general theory of the method is as follows.[2] Let ϕ be the volume containing 1 equivalent, then if F coulombs are passed, the single boundary moves through the volume $n\phi$, where n is the transport number. For Q coulombs the motion is $n\phi Q/F$, hence if V is the space swept out by the single boundary, $V = n\phi Q/F$, or:

$$n = \frac{VF}{\phi Q}.$$

If two boundaries are used, it is not necessary to measure Q. A solution of the salt AB investigated is stratified between solutions of salts $B'A$ and BA', having the same anion and kation, respectively, and lighter and denser than AB, giving the boundaries a and b, which may be seen owing to the different refractive indices of the solutions, even when these are colorless.[3] After passage of the current the boundaries move to a', b'. The ratio of the distances:

[1] *Phil. Trans.*, **184**, 337 (1893); **186**, 507 (1895); *Phil. Mag.*, **38**, 398 (1894).

[2] Cf. McInnes and Smith, *J. Am. Chem. Soc.*, **45**, 2246 (1923); *ibid.*, **46**, 1398 (1924); Lorenz and Neu, *Z. anorg. Chem.*, **116**, 45 (1921); for application to colloids see Pauli and Engel, *Z. physik. Chem.*, **126**, 247 (1927) with literature.

[3] Steele, *Phil. Trans.*, **198**, 105 (1902); *Z. physik. Chem.*, **40**, 689 (1902); Steele's work was adversely criticized by Abegg and Gaus, *Z. physik. Chem.*, **40**, 737 (1902), and by Denison, *ibid.*, **44**, 575 (1903). Denison was able to improve the method to some extent, Denison and Steele, *Phil. Trans.*, **205**, 449 (1906); *Trans. Farad. Soc.*, **5**, 165 (1909); cf. Luther in Winkelmann's Physik, IV, i, 889; Nernst, *Z. Elektrochem.*, **3**, 308 (1897). The moving boundary method was also used by Masson, *Phil. Trans.*, **192**, 331 (1899); *Z. physik. Chem.*, **29**, 501 (1899); new apparatus by MacInnes and Brighton, *J. Am. Chem. Soc.*, **47**, 994 (1925); MacInnes, Cowperthwaite and Blanchard, *ibid.*, **48**, 1909 (1926); Smith and MacInnes, *ibid.*, **47**, 1009 (1925); *ibid.*, **46**, 1398 (1924); Smith, *ibid.*, **50**, 1904 (1928).

$aa'/(aa' + bb')$ then gives the transport number of one ion. The ions B' and A' must have smaller mobilities than B and A, respectively, in order that the boundaries may remain sharp. The theoretical condition is $c/n = c'/n'$, where c = ion concentration, and n, n' refer to leading and following ions.[1]

An error in this method was pointed out by G. N. Lewis,[2] viz., the shrinkage of a vertical column of liquid when concentration changes occur at the electrodes, causing a shift in the position of the boundary. These may be allowed for in the calculation, by using the equation $n = (1/\phi)(VF/Q + \Delta v)$, where Δv is the change in volume at the electrode per faraday, but the method as a whole does not seem at present to give very satisfactory results.

The three methods used for the determination of transport numbers[3] are (i) the gravimetric method of Hittorf; (ii) the moving boundary method, (iii) from conductivity, making use of Kohlrausch's law. These have been fully discussed by Noyes and Falk.[4] The values from (i) and (ii) agree at 18° within 1 per cent for HCl, HNO_3, H_2SO_4, KCl, K_2SO_4 and NH_4Cl, but for other substances (i) gives results 2.5 to 3 per cent higher than (ii). Method (iii) gives results 1 to 3 per cent higher than (ii) for uni-univalent salts, and the second method is therefore suspected. In the case of almost all uni-univalent substances the values from (iii) at infinite dilution agree to about 1 per cent with those from (i) at 0.005 to 0.02 n. The difference falls outside the limits of error with other salts.

The migration ratios in fused salts have been investigated (see "Fused Salts"). In fused silver iodide the current is wholly carried by the $Ag^{\cdot}$ ion;[5]

[1] Kohlrausch, *Ann. Physik*, **62**, 209 (1897); Weber, *Sitz. Ber. Preuss. Akad.*, p. 567 (1897); *Z. physik. Chem.*, **4**, 182 (1889); Masson, *Z. physik. Chem.*, **29**, 501 (1899); Denison, *ibid.*, **44**, 581 (1903); Miller, *ibid.*, **69**, 436 (1909); Laue, *Z. anorg. Chem.*, **93**, 329 (1915); Lorenz and Neu, *ibid.*, **116**, 45 (1921); McInnes and Smith, *J. Am. Chem. Soc.*, **45**, 2246 (1923).

[2] *J. Am. Chem. Soc.*, **32**, 862 (1910); Noyes and Falk, *ibid.*, **33**, 1436 (1911), regard the method as unsatisfactory.

[3] Additional papers on apparatus and calculation of transport numbers: Findlay, *Chem. News*, **100**, 185 (1909); Chittock, *Proc. Cambridge Phil. Soc.*, **15**, 55 (1909) (very low concs.); Riesenfeld and Reinhold, *Z. physik. Chem.*, **68**, 440 (1909); Noyes and Stewart, *J. Am. Chem. Soc.*, **32**, 1133 (1910); Falk, *ibid.*, **32**, 1555 (1910); Drucker, *Z. Elektrochem.*, **17**, 398 (1911); **19**, 8 (1913); Dhar and Bhattacharyya, *Z. anorg. Chem.*, **82**, 141 (1913); *Proc. K. Akad. Wetens. Amsterdam*, **18**, 375 (1915) (at 0°); Strachan and Chu, *J. Am. Chem. Soc.*, **36**, 810 (1914); Kraus, *ibid.*, **36**, 35 (1914); Quagliariello and d'Agostino, *Atti R. Accad. Lincei*, **24**, i, 638, 772 (1915); Heydweiller, *Z. physik. Chem.*, **89**, 281 (1915); Drucker and Krsnjavi, *ibid.*, **62**, 731 (1908); Doumer, *Compt. rend.*, **146**, 329, 687, 894 (1908); Doumer and Guilloz, *ibid.*, **146**, 580 (1908); C. H. Griffiths, *Proc. Phys. Soc. London*, **28**, 132 (1916); Stepniczka-Marinkovic, *Monatsh.*, **36**, 831 (1915); Hopfgartner, *ibid.*, 751 ($Fe^{\cdots}$ slightly less mobile than $Fe^{\cdot\cdot}$); Krumreich, *Z. Elektrochem.*, **22**, 446 (1916); Hevesy, *ibid.*, **27**, 21 (1921) ($H^{\cdot}$ and OH'); Baborovský, *Rec. trav. Chim.*, **42**, 229 (1923); Lorenz and Posen, *Z. anorg. Chem.*, **96**, 81 (1916); Scarpa, *Nuovo Cim.*, **3**, 308 (1912); Chandler, *J. Am. Chem. Soc.*, **34**, 662 (1912); Davies and Hudleston, *J. Chem. Soc.*, **125**, 260 (1924); Holroyd and Rhodes, *ibid.*, 438; Kendall, Jette and West, *J. Am. Chem. Soc.*, **48**, 3114 (1926) and Kendall and West, *ibid.*, 2619 (Separation of isotopes); Grebe, *Phys. Rev.*, **25**, 113 (1925); Washburn, *J. Am. Chem. Soc.*, **31**, 322 (1909).

[4] *J. Am. Chem. Soc.*, **33**, 1436 (1911). Cf. Millar, *Z. physik. Chem.*, **69**, 436 (1909).

[5] O. Lehmann, *Ann. Physik*, **24**, 1 (1885); **38**, 396 (1889).

in glass the kations only carry the current.[1] The influence of non-electrolytes on transport numbers has not been very fully investigated.[2]

Hydration from Transport Experiments: If an indifferent substance is added to a solution of an electrolyte, the changes of concentration of indifferent substance around the electrodes will depend only on the transport numbers and the hydrations of anion and kation.[3] In an experiment, 0.04974 faraday passed through a solution which contained 8.108 per cent of KCl and 4.418 per cent of raffinose. At the end of the electrolysis, 103.21 gm. of anode solution contained 6.719 gm. of KCl and 4.661 gm. of raffinose. Before electrolysis $8.108 \times 4.661/4.418 = 8.553$ gm. of KCl were associated with 4.661 gm. of raffinose, hence the concentration decrease, referred to a fixed weight of raffinose, is $8.553 - 6.719 = 1.834$ gm. of KCl, equivalent to $1.834 \times 39/74.5 = 0.960$ gm. K. If the K ion had carried all the current, the transference would have been $0.04974 \times 39 = 1.940$ gm. K; hence, the "true" transport number of the potassium ion is $0.96/1.94 = 0.495$. If A and K are the numbers of molecules of water bound to anion and kation, then:

$$nA - (1 - n)K = x,$$

where n is the transport number of the anion and x the number of mols. of water transported to the anode or kathode per F. If u, v are the mobilities of the kation and anion:

$$A - (u/v)K = x/n.$$

Values of x/n have been found by Buchböck,[4] Washburn,[5] and others:

	HCl	KCl	NaCl	LiCl
x/n	− 1.42 to − 1.52	− 1.27	− 1.24	− 2.05

Remy [6] found practically the same values when the intermediate liquid was gelatinized and the changes of volume at the electrodes read off on capillary tubes. The results were corrected for electro-endosmosis, and the mobilities in the jelly were found practically the same as in solutions. On the assumption that the number of molecules of water attached to the $H^{\cdot}$ ion is 1, the relative hydrations of other ions were found to be:[7] $K^{\cdot}$, 5; $Na^{\cdot}$, 8; $Li^{\cdot}$, 14; Cl', 4.

[1] Warburg, *Ann. Physik*, **21**, 622 (1884); Warburg and Tegetmeier, *ibid.*, **35**, 455 (1888); Tegetmeier, *ibid.*, **41**, 18 (1890). Lorenz and Fausti, *Z. Elektrochem.*, **10**, 630 (1904); Lorenz, Elektrolyse geschmolzener Salze. ii, 159 ff., found $n = 0.36$ for $K^{\cdot}$ in fused $PbCl_2 + KCl$, but the method is inexact. Possibly complex ions are present.

[2] Ferguson and France, *J. Am. Chem. Soc.*, **43**, 2161 (1921); Scatchard, *ibid.*, **46**, 2353 (1924); France and Moran, *ibid.*, 19; Audubert, *Compt. rend.*, **176**, 838 (1923); Corran, *J. Am. Chem. Soc.*, **45**, 1627 (1923) finds n for KI constant up to 50 per cent sucrose, then increases slightly. Most measurements have been made by concentration cells.

[3] Nernst, *Götting. Nachr.*, 1 (1900).

[4] *Z. physik. Chem.*, **55**, 563 (1906).

[5] *Z. physik. Chem.*, **66**, 513 (1909); Washburn and Millard, *J. Am. Chem. Soc.*, **37**, 694 (1915). Baborovsky, *Rec. trav. Chim.*, **42**, 229 (1923); Riesenfeld, below.

[6] *Z. physik. Chem.*, **89**, 467, 529 (1915).

[7] Nernst, Lehrbuch, 8–10 Aufl., p. 442; Remy and Marregold, *Z. physik. Chem.*, **118**, 161 (1925); Remy, *ibid.*, **89**, 529 (1915) used the electroendosmose method; *Trans. Farad. Soc.*,

Riesenfeld and Reinhold[1] assume that the values found in very dilute solutions are the "true" transport numbers, whilst those found in more concentrated solutions require correction for the transport of water by the ions.[2] Consider a solution of 1 equiv. of electrolyte in a mols. of water and let 1 F pass. At the anode, a mols. H_2O will now contain $1 + n$ equiv. electrolyte, where n is the "observed" transport number. In $a + x$ mols. of H_2O there will be $1 + n + (x/a)$ equiv. of electrolyte. If n_0 is the true transport number and A and K the numbers of mols. H_2O attached to anion and kation, respectively, then, as before:

$$n_0 A - (1 - n_0)K = x.$$

If x is positive at the anode, then in $a + x$ mols. of water after electrolysis there will be $1 + n_0$ equiv. of electrolyte. Thus:

$$1 + n_0 = 1 + n + (x/a), \qquad \text{or} \qquad n = n_0 + (x/a),$$

or, if $c = 1/a$ = concentration,

$$-dn/dc = x,$$

giving x from the curve $n = f(c)$. From these curves the following conclusions may be drawn:

(i) If the anion is more mobile than the kation at high dilutions, the latter is usually more hydrated than the former.

(ii) In such a case the transport number increases at first with increasing concentration; in the opposite case it decreases.

The degree of hydration of the ion may be calculated by combining the above equation with the assumption that the hydrated ion is surrounded by a spherical shell of water molecules, the volume of which can be calculated from Stokes's law.[3] If the volume of the ion can be neglected in comparison with that of the water (strong hydration), the volume of the latter, and thence

23, 381 (1927); Remy and Reisener, *Z. physik. Chem.*, **124**, 41, 394 (1926); **126**, 161 (1927); Dhar, *Z. Elektrochem.*, **31**, 261 (1925); *ibid.*, **32**, 596 (1925); Baborovsky, *Z. physik. Chem.*, **129**, 129 (1927); Baborovsky and Wagner, *ibid.*, **131**, 129 (1928); Velisek, *Chem. Listy*, **20**, 242 (1926); *C.A.* 1926, 3117.

[1] *Z. physik. Chem.*, **66**, 672 (1909).

[2] G. N. Lewis, *J. Am. Chem. Soc.*, **32**, 862 (1910), shows that the results of the moving boundary method, corrected for changes of volume, give the Hittorf transport numbers, not the "true" transport numbers.

[3] Cf. Lungo, *Nuovo Cim.*, **16**, ii, 173 (1918); Lorenz, *Z. Elektrochem.*, **26**, 424 (1920); *Z. physik. Chem.*, **73**, 252 (1910); cf. Dhar, *Z. Elektrochem.*, **19**, 748 (1913); Lindemann, *Trans. Farad. Soc.*, **15**, 166 (1919); Lorenz, *Z. anorg. Chem.*, **94**, 265 (1916); Lorenz and Posen, *ibid.*, **96**, 81, 217, 231 (1916); Hevesy, *Jahrb. Radioakt. Elektronik*, **2**, 419 (1914); **13**, 273 (1916); *Koll. Z.*, **21**, 129 (1917); Lorenz and Scheuermann, *Z. anorg. Chem.*, **117**, 140 (1921); Schmick, *Z. Physik*, **24**, 56 (1924); Ulich, *Trans. Farad. Soc.*, **23**, 388 (1927); Lattey, *Phil. Mag.*, **6**, 258 (1928); modified Stokes's law, Born, *Z. Physik*, **1**, 221 (1920); *Z. Elektrochem.*, **26**, 401 (1920); Schmick, *Z. Physik*, **24**, 36 (1924); Guyemant, *ibid.*, **30**, 240 (1924); Lenard, Weick and Mayer, *Ann. Physik*, **61**, 665 (1920); Kraus, Electrically Conducting Systems, p. 203; cf. Dummer, *Z. anorg. Chem.*, **109**, 31 (1919); S. W. J. Smith, *Proc. Phys. Soc. London*, **28**, 16 (1916); Bousfield, *Z. physik. Chem.*, **53**, 257 (1905); *Proc. Roy. Soc.*, **74**, 563 (1905).

the hydration, can be found. If l_1, l_2 are the mobilities of two ions and r_1, r_2 their radii (including water envelopes), then Stokes's law gives:

$$l_1/l_2 = r_2/r_1.$$

But if A_1, A_2 are the numbers of molecules of water attached to the ions:

$$A_1/A_2 = r_1^3/r_2^3; \qquad \text{hence} \qquad A_1/A_2 = l_2^3/l_1^3.$$

In this way the following values are found, at infinite dilution: $H^{\cdot}$, 0; OH', 10; $K^{\cdot}$, Cl', Br', I', $\frac{1}{2}SO_4''$, 20; NO_3', 25; $Ag^{\cdot}$, ClO_3', 35; $\frac{1}{2}Cd$, $\frac{1}{2}Cu$, 55; $Na^{\cdot}$, 70; Li, 150.

With increasing concentration of electrolyte the hydration decreases. A second method,[1] depending on the use of concentration cells, has given no satisfactory results. In other calculations, Lorenz arrived at the conclusion that the values of the ionic radii calculated by the formula: $r = 8.15 \times 10^{-9}/l\eta$ (r in cm.; l in Kohlrausch units; η = viscosity in absolute units) are approximately the same as the radii of the atoms calculated by the Reinganum formula, in the case of kations, except for lithium, the ion of which had twice the radius of the atom and was, therefore, in all probability hydrated. The diameters of ions which, on the basis of transport experiments, were supposed to be hydrated, were about the same as those of the atoms. The calculations break down with inorganic anions. Large organic ions are not hydrated, or at any rate less so than inorganic ions. Born assumed that the Stokes-Einstein equation for the motion of spheres in a viscous medium applies even to small ions, any deviations being due to electrical interaction between the charge and the solvent molecules, an effect which increases as the ion becomes smaller, whilst then the fluid viscosity diminishes. The resistance to the motion of the ion thus reached a minimum value.

Ulich, who postulates a firmly adhering solvent envelope around the ion and the validity of Stokes's law, calculates the value of $4/3\pi r^3 N$ (N = Avogadro's constant) from the value of r obtained by the above formula, and subtracts from this the value of $4/3N\pi r_0^3$, r_0 being the ionic radius as calculated from crystal lattice measurements. The difference, v_s, is then regarded as the volume occupied by the solvent envelope. By simply dividing this by the molar volume of the solvent we should, according to Ulich, get too small a value for the solvation number, on account of the compression of the solvent by the electrostatic forces. He, therefore, divides v_s by the experimentally found true molar volumes of organic (non-solvated) kations as found by Lorenz, and thus finds for each v_s "the mean number of atoms of those organic molecules, the true molecular volume (not including any intramolecular spaces) of which is equal to v_s; we presume that we thereby determine likewise the number of atoms within the envelope of an ion." Dividing this by the number of atoms in the molecule of solvent gives the solvation number. The results show that the solvent layer formed around the ion is probably not more than one molecule thick, and the iodide ion is not solvated.

[1] Reinhold, *Z. Elektrochem.*, **14**, 765 (1908); cf. Riesenfeld and Reinhold, *Z. physik. Chem.*, **68**, 459 (1910). Cf. Lenard, Weick and Mayer, *Ann. Physik*, **61**, 665 (1920).

It will be seen that there is no agreement among the solvation numbers found by different methods, and the same is true of the results of earlier work.[1]

The abnormally high mobilities of $H^{\cdot}$ and OH' ions is perhaps due, at least in part, to their low hydration. The suggestion has been made[2] that the hydrogen ion in aqueous solutions is really the oxonium ion, $H_3O^{\cdot}$, having the same relation to oxygen as $NH_4^{\cdot}$ to ammonia. Others[3] attribute the abnormal mobilities of $H^{\cdot}$ and OH' to Grotthus conduction. The free energy of hydration of ions[4] has been calculated from the difference between the energies required to charge an ion in a vacuum and that required in water, allowance being made for the compression of the solvent around the ion and the change in dielectric constant.

	H^+	Zn^{++}	Na^+	K^+	Cl^-	I^-
$r \times 10^8$ cm.	<0.5	1.04	1.505	1.873	2.24	2.60
F in k. cal.	250	525	99	82	70	61

Effect of Temperature on Ionic Mobility: Kohlrausch assumed that the formulæ giving the effect of temperature on equivalent conductance can be extended to the mobilities of the separate ions.[5] For univalent ions those with small mobilities have large temperature coefficients. Lindemann[6] connects the temperature coefficient with the change in the mean free path of the ions. According to Kohlrausch[7] the following relations between the temperature coefficient α and the mobility l hold good in aqueous solutions:

[1] H. C. Jones and collaborators, beginning in 1899; summarized to 1908 by Jones, *Am. Chem. J.*, **41**, 19 (1909); Jones, Hydrates in Aqueous Solutions, *Carnegie Inst. Pub.*, No. 60 (1907); Ordeman, *ibid.*, **260**, 119 (1918); criticized by Serkoff, *J. Russ. Phys. Chem. Soc.*, **42**, 1 (1910); see also Jones, etc., *Am. Chem. J.*, **49**, 265 (1913); *J. Franklin Inst.*, **173**, 217 (1912); **176**, 479, 677 (1913); The Nature of Solution, H. C. Jones, London, 1917; Baur, Von den Hydraten in wässriger Lösung, Stuttgart, 1903; critical summary by Dhar, *Z. Elektrochem.*, **20**, 57 (1914); the transport method is criticized by Isgarischev and Berkmann, *Z. Elektrochem.*, **28**, 40 (1922); Aschkenasi, *ibid.*, **28**, 106 (1922); Bjerrum, *Z. anorg. Chem.*, **109**, 275 (1920); Schreiner, *ibid.*, **121**, 321 (1922). Sugden, *J. Chem. Soc.*, 1926, p. 174; Schreiner, *Z. anorg. Chem.*, **135**, 333 (1924). Newberry, *J. Chem. Soc.*, **111**, 470 (1917). concludes from overvoltage measurements that only $H^{\cdot}$, OH', $Fe^{\cdot\cdot\cdot}$, $Ni^{\cdot\cdot}$ and $Co^{\cdot\cdot}$ (perhaps Pt, etc.) ions are hydrated, and criticizes methods of determination of hydration. At the present time it is hardly certain that ions *are* hydrated, and the extent of hydration cannot yet be expressed numerically with any accuracy.

[2] Lapworth, *J. Chem. Soc.*, **93**, 2187 (1908).

[3] Danneel, *Z. Elektrochem.*, **11**, 249 (1905); Hantzsch and Caldwell, *Z. physik. Chem.*, **58**, 575 (1907); Ghosh, *J. Chem. Soc.*, **113**, 790 (1918); criticized by Kraus, Electrically Conducting Systems, p. 209.

[4] Webb, *J. Am. Chem. Soc.*, **48**, 2589 (1926).

[5] Leitvermögen, p. 128; values see this book, p. 673.

[6] *Z. physik. Chem.*, **110**, 394 (1924).

[7] *Ann. Physik*, **50**, 385 (1893); *Sitz. Ber. Preuss. Akad.*, p. 581 (1902); *Proc. Roy. Soc.*, **71**, 338 (1903); *Z. Elektrochem.*, **14**, 129 (1908); Leitvermögen, p. 128; *Sitz.-ber. preuss. Akad.*, p. 1033 (1901).

$$\alpha = 0.0136 + 0.67/(18.5 + l) = 0.0134 + 0.640/l - 6.94/l^2$$
$$= 0.0065 + 0.0683(1/l)^{0.3545}$$
$$= 0.0348/(ln\, l - 0.207).$$

One consequence of the small temperature coefficients of very mobile ions is that, with rise of temperature, the mobilities of all ions should tend to become equal, and the transport numbers then tend to equal 0.5. The parallellism between temperature coefficients of conductance and viscosity has been referred to previously. If we calculate from the equation:

$$\kappa_t = \kappa_{18}[1 + \alpha(t - 18) + (\alpha - 0.0177).0.0177(t - 18)^2]$$

the temperature at which $\kappa_t = 0$, we find $-39°$ C. The empirical formula for the fluidity of water as a function of temperature given by Heydweiller would give infinite viscosity at $-34°$, an interesting coincidence which suggests that the mobility is perhaps that of the hydrated ion, so that there is then friction between water and water. Noyes and Falk [1] have discussed fully the effect of temperature on transport number, and conclude that if the transport number is larger than 0.5 it invariably diminishes with rise of temperature, and if it is less than 0.5 it invariably increases. This agrees with the above result.

Diffusion of Electrolytes: The diffusion constant D of an electrolyte is connected with the mobilities of its ions by the equation: [2]

$$D_t = 0.044856\frac{uv}{u + v}[1 + 0.0034(t - 18)],$$

where u, v are the mobilities at $t°$,[3] and D is expressed in the usual units (cm./day).

The following table [4] shows the agreement between observed and calculated values of D at 18°.

TABLE XII

Diffusion Coefficients of Electrolytes (cm./day) at 18° C.

	D obs.	D calc.		D obs.	D calc.
HCl	2.30	2.43	KNO_3	1.30	1.39
HNO_3	2.22	2.26	NaCl	1.11	1.18
KOH	1.85	2.07	$NaNO_3$	1.03	1.13
NaOH	1.40	1.55	H.COONa	0.95	1.02
NH_4Cl	1.33	1.44	CH_3COONa	0.78	0.88

[1] *J. Am. Chem. Soc.*, **33**, 1436 (1911).

[2] Nernst, *Z. physik. Chem.*, **2**, 613 (1888); **4**, 129 (1889); Lehrbuch, 8–10 Aufl., 429; Arrhenius, *ibid.*, **10**, 51 (1892); Abegg and Bose, *ibid.*, **30**, 545 (1899); Euler, *Ann. Physik*, **63**, 273 (1897); Behn, *ibid.*, **62**, 54 (1897); Planck, *ibid.*, **40**, 561 (1890); Larmor, Æther and Matter, Cambridge, p. 291 (1900); *Phil. Trans.*, **185**, 815 (1894); Donnan, *Phil. Mag.*, **45**, 529 (1898); deduction, see Whetham, Theory of Solution, 1902, chap. 13.

[3] Winkelmann, Physik, IV, p. 437.

[4] Measurements by Scheffer, *Ber.*, **15**, 788 (1882); **16**, 1903 (1883); *Z. physik. Chem.*, **2**, 390 (1885); cf. also Clack, *Phil. Mag.*, **16**, 863 (1908); Vanzetti, *Atti R. Accad. Lincei*, **18**,

The relation $DM^{1/2}$ = const., where M = molecular weight, has been found by Thovert.[1]

Conductivity and Chemical Constitution: A number of regularities have been pointed out in the relations between conductivity and chemical constitution. These include[2] comparisons between ionic mobilities and between ionization constants, K, of the Ostwald dilution law.

Bredig[3] found that the mobility of elementary ions is a periodic function of their atomic weights, and rises with atomic weight in each family of elements. Analogous atoms, with atomic weights exceeding 35, have approximately equal mobilities. Thus, the mobilities at infinite dilution of $\frac{1}{2}Mg^{\cdot\cdot}$, $\frac{1}{2}Ca^{\cdot\cdot}$, $\frac{1}{2}Sr^{\cdot\cdot}$ and $\frac{1}{2}Ba^{\cdot\cdot}$, at 25°, are 62, 66, 67 and 68, respectively; those for $Li^{\cdot}$, $Na^{\cdot}$, $K^{\cdot}$, $Rb^{\cdot}$ and $Cs^{\cdot}$ are, respectively: 42.6, 52.6, 75.5, 78.6 and 78.8. Isomeric and metameric anions have the same mobility: the equivalent mobilities of ortho-, meta- and para-toluic, and phenylacetic acids are 32.0, 32.1, 31.7 and 31.9, respectively, phenylacetic acid being metameric with the other three isomeric acids. This rule does not hold for kations.

The greater the number of atoms in an ion the smaller the mobility (Bredig, *loc. cit.*), provided anions are compared with anions, and kations with kations. The rule holds less rigidly among kations. The mobility of an ion is reduced by substitution of H by halogen, NH_2, NO_2, and sometimes CH_3.

Inorganic acids differ from organic acids[4] in that they are strong electrolytes in aqueous solution (except H_2CO_3, H_2S, HCN) and do not obey Ostwald's dilution law. Little is known as to their constitution, but it appears that addition of oxygen or sulphur assists the formation of ions ($H_2S_4O_6$ is as strongly ionized as HCl).

Organic acids have been well studied.[5] The ionization constant K of fatty acids decreases as the series is ascended, but the substitution of successive CH_3 groups does not cause a constant decrease. Substitution of H by Cl, Br, and I causes a large increase of K, the magnitude decreasing in the order given. The substitution of a second atom of Cl has less effect than the first, and a third less than the second. The effect of replacing Cl by CN is still further to increase K, and this is supposed to indicate that the CN group in HCN (a very weak acid) is differently constituted from that in cyanacetic acid. Substitution by halogen in the α position produces a greater effect on

ii, 229 (1909); Scarpa, *Nuovo Cim.*, **20**, 212 (1910); Öholm, *Medd. K. Vetensk. Nobel Inst.*, **2**, No. 22 (1912); *ibid.*, *Finske Kemistamfundets Medd.*, **30**, 69 (1921); Griffiths, *Proc. Phys. Soc. London*, **29**, 159 (1917).

[1] *Compt. rend.*, **150**, 270 (1910); attempts to determine ionic hydration from diffusion measurements have been made by McPhail Smith, *J. Am. Chem. Soc.*, **37**, 722 (1915).

[2] Cf. Lehfeldt, Electrochemistry, London, 1908, p. 93 f. (by T. S. Moore); Ostwald, Lehrbuch, II, 1, 674 f.

[3] *Z. physik. Chem.*, **13**, 191 (1894); cf. Lorenz and Posen, *Z. anorg. Chem.*, **96**, 217 (1916).

[4] Effects of substitution in organic acids; summary by Wegscheider, *Monatsh.*, **23**, 287 (1902); Nernst, Lehrbuch, 8–10 Aufl., p. 583.

[5] Ostwald, *J. prakt. Chem.*, **31**, 433 (1885); *Z. physik. Chem.*, **3**, 170 (1889); Walker, *ibid.*, **4**, 319 (1889); Bethmann, *ibid.*, **5**, 385 (1890); Bader, *ibid.*, **6**, 289 (1890); Walden, *ibid.*, **8**, 433 (1891); Bredig, *ibid.*, **13**, 289 (1894); Jones, Lloyd and Wiesel, *J. Am. Chem. Soc.*, **38**, 121 (1916) (alcohol solutions); MacInnes, *ibid.*, **50**, 2587 (1925).

ionization than in the β position. Similar results have been found in the substitution of H by OH in all acids, fatty and aromatic, except in the case of *p*-substitution in the benzene nucleus.

Unsaturated acids ionize more readily than the corresponding saturated acids different isomers (e.g., crotonic and isocrotonic acids) have different ionizations.

The aromatic acids show much greater regularity than aliphatic. In the case of substitution in the nucleus, the groups CH_3, OH, NO_2, Cl increase K, the effect being greater in the ortho- than in the meta- and para-positions; NH_2 decreases K, the greatest effect being in the ortho- and the least in the meta-position. In the case of two substituents in the same acid, the actual ionization is less than the value calculated on the assumption that each behaves independently, although in the case of α-dibromopropionic acid the discrepancy is not large. The same holds in general for aromatic acids.

The transition of acids from the benzene to the pyridine series is accompanied by decrease in the ionization constant.

In the case of dibasic acids [1] the first ionization constant, calculated from conductivity, is equal to the sum of two ionization constants, one for each carboxyl group, which are equal if the acid is symmetrical. Of two dibasic acids which are analogous, the one with a larger second ionization constant appears to have a smaller first ionization constant (Ostwald).

Conductivity measurements have played an important part in the elucidation of the constitution of pseudo-acids.[2]

Organic bases do not exhibit such regularities as acids; [3] secondary bases are usually stronger than primary or tertiary.

Neutral salts, organic and inorganic, are in general highly ionized, even if they are of weak acids or bases, and approximately to the same extent at equal dilutions. Some salts, e.g., $HgCl_2$, $HgCy_2$, are only slightly ionized. By the application of the Ostwald-Bredig dilution rule (p. 653) it has been found that KH_2PO_4 and KH_2AsO_4 ionize as monobasic acids.[4]

Isohydric Solutions: Two solutions containing salts with a common ion are said to be *isohydric* when the concentration of that ion is the same in both solutions. The conductivity of a mixture of such solutions is the mean of the conductivities of the separate solutions.[5] Consider the first salt AB. The mass law gives

$$K_1 = (A')_1(B')/V_1(AB),$$

where (A'), (B'), etc., are the actual numbers of mols. contained in a volume V

[1] Cf. Meldrum, *J. Phys. Chem.*, **15**, 474 (1911).

[2] Hantzsch, *Ber.*, **32**, 575 (1899); Hantzsch and Kalb, *ibid.*, **32**, 3109 (1899).

[3] Summary: Bredig, *Z. physik. Chem.*, **13**, 289 (1894).

[4] Complex and double salts: see Jones and Mackay, *Am. Chem. J.*, **19**, 83 (1897); Archibald, *Trans. Nova Scotia Inst. Sci.*, **9**, 307 (1891); Morgan, *Z. physik. Chem.*, **17**, 513 (1895); Steele, *Phil. Trans.*, **198**, 105 (1902); Werner and Miolati, *Z. physik. Chem.*, **12**, 35 (1893); **14**, 506 (1894). Except at high dilutions, complex ions appear to exist in solutions of double salts.

[5] Arrhenius, *Ann. Physik*, **30**, 51 (1887); *Z. physik. Chem.*, **2**, 284 (1888); **5**, 1 (1890).

of solution. Similarly for the second salt AC:

$$K_2 = (A')_2(C')/V_2(AC).$$

In general $(A')_1$ is not equal to $(A')_2$, since the ionizations are unequal.

When the solutions are mixed the concentration of the common ion in the mixture is seen to be $((A')_1 + (A')_2)/(V_1 + V_2)$ and this will be in equilibrium with the ionization of the salt AB when the equation:

$$K_1 = (B')[(A')_1 + (A')_2]/(V_1 + V_2)(AB) = (B').(A')_1/V_1(AB)$$

is satisfied, and with the ionization of the salt AC when the equation:

$$K_2 = (C')[(A')_1 + (A')_2]/(V_1 + V_2)(AC) = (C').(A')_2/V_2(AC)$$

is satisfied. By division:

$$(A')_1/V_1 = (A')_2/V_2.$$

On mixing such solutions in any proportions no displacement of the dissociation occurs, and hence the conductivity of the mixture is the mean of that of the solutions, provided the concentrations of the common ion were equal in the separate solutions.[1] Let α_1, α_2 be the degrees of ionization of AB and AC in two separate solutions of dilutions v_1 and v_2 isohydric with the mixed solution in which the dilutions of the separate salts are V_1 and V_2 in the mixed solution. Then we find the equations:

$$[A'] = \frac{\alpha_1}{V_1} + \frac{\alpha_2}{V_2},$$

$$\frac{\alpha_1^2}{(1-\alpha_1)v_1} = K_1, \qquad \frac{\alpha_2^2}{(1-\alpha_2)v_2} = K_2,$$

$$[A'] = \frac{\alpha_1}{v_1} = \frac{\alpha_2}{v_2} = \frac{K_1(1-\alpha_1)}{\alpha_1} = \frac{K_2(1-\alpha_2)}{\alpha_2},$$

which when combined give cubic equations for α_1 and α_2, the solutions of which give the ion concentrations in the mixed solution. In the case in which α is small compared with 1 (e.g., weak acids in solutions not too dilute) the solutions take the simple forms:

$$\alpha_1 = K_1\sqrt{\frac{V_1V_2}{V_1K_2 + V_2K_1}},$$

$$\alpha_2 = K_2\sqrt{\frac{V_1V_2}{V_1K_2 + V_2K_1}}.$$

The conductivity of mixtures of acids varies considerably with dilution. Arrhenius[2] found that the ionization of a weak acid in presence of one of its

[1] Cf. Arrhenius, *Z. physik. Chem.*, **31**, 218 (1899); Bray and Hunt, *J. Am. Chem. Soc.*, **33**, 781 (1911). Wakemann, *Z. physik. Chem.*, **15**, 159 (1894).

[2] *Z. physik. Chem.*, **5**, 1 (1890). Cf. Dorochevski and Fridman, *J. Russ. Phys. Chem. Soc.*, **47**, 1615 (1915); *Chem. Abs.*, **10**, 2822 (1916).

salts is inversely proportional to the amount of salt present. Consider the addition of sodium acetate to acetic acid. For acetic acid $K = 1.8 \times 10^{-5}$ at 25°. In 1 N solution we thus find from the equation $x^2/(1 - x)V = K$ that

$$x = [H^{\cdot}] = 0.004.$$

But

$$[H^{\cdot}] = K[HAc']/[Ac'].$$

Let sodium acetate be added to concentration 1 N. At this concentration the salt is 50 per cent ionized

$$\therefore \quad [Ac'] = 0.5.$$

We neglect the very small concentration of $[Ac']$ from the acetic acid and also take $[HAc] = 1$

$$\therefore \quad [H^{\cdot}] = \frac{K.1}{0.5} = 3.6 \times 10^{-5} = 0.00004 \text{ approx.}$$

By the addition of the acetate the $[H]$ ion concentration is reduced to one per cent of its former value. (See vol. 2, on Buffer Solutions.)

The case of solutions containing two binary electrolytes with no common ion is difficult to work out. Arrhenius (*loc. cit.*) showed that when a weak acid and several strong electrolytes exist in the same solution, the respective degrees of dissociation may be calculated as though the dissociated part of the particular electrolyte were a dissociated part of a salt of the weak acid.

Sherrill [1] finds, in particular cases, that if the concentrations of the separate ions in mixtures of salts with no common ion are calculated by the equation

$$[A] \times [B]/A_xB_y = K(\sum i)^{2-n},$$

where $\sum i$ = *total* ion concentration, the results are accurate to 0.5 per cent at 0.2 $n.$, and 0.25 per cent at 0.1 n. The ion concentrations were determined by conductivity.

Mackay [2] tested the assumption of Arrhenius that in a solution containing two salts with a common ion, each salt has a degree of ionization equal to that which it would have when present alone in a solution in which its ions have a concentration equivalent to that of the common ion in the mixed solutions. In a solution containing ammonium sulphate and chloride in 0.2009 n. concentration, the partial conductivity of the chloride was 2 per cent larger than the calculated, and that of the sulphate 5.2 per cent larger. The partial conductivities were found from the transport number and conductivity. Bray and Hunt [3] found in mixtures of hydrogen and sodium chlorides that the observed conductivities in solutions 0.001 to 0.2 n. were always 1.6 per cent less than those calculated in 0.1 n. solutions of each substance, the difference diminishing as the concentration fell. It was suggested that the conductance

[1] *J. Am. Chem. Soc.*, **32**, 741 (1910).
[2] *J. Am. Chem. Soc.*, **33**, 308 (1911). Egner, *Medd. K. Vet. Nobel Inst.*, 6, No. 5, 1 (1925).
[3] *J. Am. Chem. Soc.*, **33**, 781 (1911).

of an ion may depend on its actual concentration rather than on the total ion concentration. The measured and calculated values agreed on this assumption and on the assumption that the ionizations of HCl and KCl are equal.[1]

Doroschevski and Dvorshantschik[2] investigated the conductivities of mixtures of aqueous solutions of sodium and potassium salts, and salts of alkaline earth metals. The isohydric principle was confirmed, when the formula of Barmwater[3] for the ionization was used. The results with sulphates and carbonates agreed with the formula $\kappa = A - a/v^{1/8}$, where v = dilution, and A and a are constants. The separate salts of the alkaline earth metals obey the formula $\kappa = A - a/v^{1/4}$, whilst KI solution agrees with the formula $\kappa = A - a/v^{1/3}$.

Kraus[4] finds that the isohydric principle when applied to mixtures of salts leads to

$$C_i^2/C_u = f(\sum C_i),$$

where $f(\sum C_i)$ is any explicit function of the sum of the ion concentrations, including all ions.[5] As the concentration of the second electrolyte increases, the function,

$$P_i/C_u = fP_i,$$

where P_i is the ionic product, reduces in the limit to the same form as the function resulting from the isohydric principle. The values for conductivity for mixtures of NaCl and HCl agree better with the experimental values than those calculated from the isohydric principle, and the equation $P_i/C_u = f(\sum C_i)$ is less accurate than $P_i/C_u = fP_i$.[6]

Stearn[7] finds the conductivities of mixtures of salts (halides of K and Na; concentrations 0.1 − 4.0 *n.*; 25° C.) less than those calculated, and that they increase with total salt concentration, and with increase of the ratio Na/K in the mixture. They decreased with increase in the ratio Cl/I. Complex formation is suggested.

Hydrolysis: In virtue of its slight ionization, pure water is capable of acting either as a weak acid or as a weak base:

$$H_2O \rightleftharpoons H^{\cdot} + OH'.$$

On the assumption that the mass law holds we have:

$$K[H_2O] = [H^{\cdot}][OH'] = K_w,$$

since the active mass of the water is constant. K_w is called the *ionization*, or

[1] See also Andreeff and Saposhnikoff, *J. Russ. Phys. Chem. Soc.*, **44**, 895 (1912); *Chem. Abs.*, **6**, 2878 (1912); Drucker, Gifford, Gomez, Guzman and Kasansky, *Z. Elektrochem.*, **19**, 797 (1913); Thomas and Baldwin, *J. Am. Chem. Soc.*, **41**, 1981 (1919).

[2] *J. Russ. Phys. Chem. Soc.*, **45**, 1174 (1913); *Chem. Abs.*, **8**, 288 (1914); **46**, 371, 419 (1914); *Chem. Abs.*, **8**, 2515 (1914).

[3] See below; *Z. physik. Chem.*, **28**, 115, 424 (1899).

[4] *J. Am. Chem. Soc.*, **43**, 2507 (1921).

[5] Arrhenius, *Z. physik. Chem.*, **31**, 218 (1899).

[6] Kraus, Electrically Conducting Systems, p. 222.

[7] *J. Am. Chem. Soc.*, **31**, 218 (1922).

dissociation, constant of water. In pure water $[H^{\cdot}] = [OH'] = c$, and thus $K_w = c^2$. The value of c, and therefore of K_w, has been found in several ways.[1]

(i) E.M.F. of the oxy-hydrogen cell (see Chapter XII).[2] This gave $K_w = 0.64 \times 10^{-14}$ at 19° and 1.42×10^{-14} at 25–26°. In pure water $[H^{\cdot}] = [OH'] = K_w^{1/2}$.

(ii) The conductivity of pure water. Kohlrausch and Heydweiller (see p. 647 found, after correcting for traces of impurity, $\kappa = 0.0384 \times 10^{-6}$ at 18°, from which $K_w = 0.61 \times 10^{-14}$. For, $\kappa = n(u + v)$, where n = no. of ions, i.e., $0.0384 \times 10^{-6} = n(318 + 174)$ or $n^2 = [H^{\cdot}] \times [OH'] = K_w = 0.61 \times 10^{-14}$.

(iii) Hydrolysis of esters by $H^{\cdot}$ and OH' ions. Wijs [3] by the hydrolysis of methyl acetate with pure water, using the results on the relative rates of hydrolysis with $H^{\cdot}$ and OH' ions, found $K_w = 1.44 \times 10^{-14}$ at 25°.

(iv) Hydrolysis of salts; the theory is given below. By this method Arrhenius [4] calculated $K_w = 1.21 \times 10^{-14}$ at 25°.

(v) Mutarotation of dextrose in aqueous, acid, or alkaline solutions.[5]

(vi) Hydrogen potential of acid or alkaline solutions.[6]

The value of K_w increases very rapidly with rise of temperature.[7] The heat of ionization is expressed by the formula:

$$Q = 27857.5 - 48.5T,$$

and K_w is 0.116×10^{-14} at 0° C., 0.281×10^{-14} at 10° C., 58.2×10^{-14} at 100° C., and 525×10^{-14} at 200° C. Noyes, Kato and Sosman [8] found that the ionization of pure water increased very rapidly with temperature between 0° C. and 100° C., less rapidly between 100° C. and 218° C., passed through a maximum between 250° C. and 275° C., and then decreased.

Consider the ionization of a weak acid, to which the law of mass action may be applied:

$$K_a = [H^{\cdot}][A']/[HA].$$

The value of $[H^{\cdot}]$ will usually exceed the value for pure water, i.e., about 1×10^{-7}, but in the dilute solution the relation $K_w = [H^{\cdot}][OH']$ must always be satisfied, from which it follows that $[OH']$ must be very much less

[1] Nernst, Lehrbuch, 8–10 Aufl., p. 589; Beans and Oakes, *J. Am. Chem. Soc.*, **42**, 2116 (1920).

[2] Ostwald, *Z. physik. Chem.*, **11**, 521 (1893); Arrhenius, *ibid.*, 805; Nernst, *ibid.*, **14**, 155 (1894); Lorenz and Böhi, *ibid.*, **66**, 733 (1909); Lewis, Brighton and Sebastian, *J. Am. Chem. Soc.*, **39**, 2245 (1917), find $K_w = 1.012.10^{-14}$ at 25° by calculation; Sörensen, *Biochem. Z.*, **21**, 131 (1909) finds $K_w = 0.73 \times 10^{-14}$ at 18°; Michaelis, Die Wasserstoffionkonzentration, Berlin, 1914, p. 8, gives a table of values of K_w for temperatures from 16° to 40°.

[3] *Z. physik. Chem.*, **12**, 514 (1893).

[4] *Z. physik. Chem.*, **11**, 805 (1893); cf. Bray, *J. Am. Chem. Soc.*, **32**, 932 (1910); Seyler and Lloyd, *J. Chem. Soc.*, **111**, 138 (1917).

[5] Hudson, *J. Am. Chem. Soc.*, **31**, 1136 (1909); not an accurate method.

[6] Frary and Nietz, *J. Am. Chem. Soc.*, **37**, 2263 (1915); $K_w = 1.76 \times 10^{-14}$ at 25°.

[7] Heydweiller, *Ann. Physik*, **28**, 503 (1909).

[8] *J. Am. Chem. Soc.*, **32**, 159 (1910).

than 10^{-7}. The electro-neutrality principle gives: $[H^{\cdot}] = [OH'] + [A']$. Hence:

$$[H^{\cdot}] = K_w/[H^{\cdot}] + K_a[HA]/[H^{\cdot}];$$

$$\therefore \quad [H^{\cdot}]^2 = K_w + K_a[HA].$$

This equation is exact; usually K_w is negligible in comparison with K_a, so that we have approximately:

$$K_a = [H^{\cdot}]^2/[HA].$$

A similar expression can be deduced for bases: $K_b = [OH']^2/[BOH]$.

When we have to deal with solutions of salts of weak acids and bases, then *hydrolysis* occurs, i.e., the salt is decomposed by water with production of free acid and base:

$$AB + H_2O \rightleftharpoons HA + BOH \rightleftharpoons H^{\cdot} + A' + B^{\cdot} + OH'.$$

The result is easily detected qualitatively, since salts are nearly always highly ionized, and the anion or kation of the salt will combine with $H^{\cdot}$ or OH' ions from the water to form nearly unionized acid or base, leaving an excess of OH' or $H^{\cdot}$ ions, respectively, in the solution, which give it an alkaline or acid reaction.

Three cases must be considered:

(i) *Salt of a strong acid and a weak base* (e.g., aniline hydrochloride):

$$AB + H_2O \rightleftharpoons HA + BOH \rightleftharpoons H^{\cdot} + A' + BOH,$$

the acid HA being largely, and the base BOH hardly at all, ionized.

The law of mass action gives:

$$[BOH][HA]/[AB][H_2O] = \text{constant},$$

or, since $[H_2O]$ is practically constant:

$$[BOH][HA]/[AB] = \text{base} \times \text{acid/salt} = K_h,$$

where K_h is the *hydrolysis constant.* K_h is defined in a way independent of the ionic theory. The decomposition of salts by water was studied by H. Rose in 1851.[1]

If the concentration of AB is 1 mol. in v liters, then, when equilibrium is attained, we have, if x is the degree of hydrolysis:

$$[HA] = x/v, \qquad [BOH] = x/v, \qquad \text{and} \qquad [AB] = (1 - x)/v,$$

$$K_w = [H^{\cdot}][OH']; \qquad \text{hence} \qquad [OH'] = K_w/[H^{\cdot}] = K_w v/x,$$

the acid HA and salt AB being completely ionized, giving a $H^{\cdot}$ concentration of x/v = acid concentration; the base is assumed non-ionized. (The presence

[1] *Ann. Physik*, **82**, 545 (1851); H. E. Armstrong, *J. Chem. Soc.*, **45**, 1418 (1884); Lundén *Sammlung chem. u. chem. techn. Vorträge*, **16** (1909).

of the ion $B^{\cdot}$ of the salt will drive back the ionization of the weak base.) If $K_b = [B^{\cdot}][OH']/[BOH]$, then:

$$K_b = \left(v\frac{K_w}{x}\cdot\frac{1-x}{v}\right)\frac{v}{x} = \frac{K_w(1-x)v}{x^2},$$

so that:

$$K_w/K_b = x^2/(1-x)v.$$

The hydrolysis calculated from the equation $AB + H_2O = HA + BOH$ gives the constant:

$$K_h = [HA][BOH]/[AB] = \frac{x}{v}\cdot\frac{x}{v}\Big/\frac{1-x}{v} = x^2/(1-x)v.$$

Hence

$$K_w/K_b = K_h.$$

Also,

$$x = -\frac{vK_w}{2K_b} \pm \sqrt{\frac{v^2}{4}\left(\frac{K_w}{K_b}\right)^2 + \frac{vK_w}{K_b}}.$$

In many cases K_b is much larger than K_w, so that the ratio K_w/K_b is very small. The expression then reduces to:

$$x = \sqrt{vK_w/K_b} = \text{const.} \times \sqrt{v},$$

so that the hydrolysis of a salt of a weak base with a strong acid is proportional to the square root of the dilution, and is easily calculated from the values of K_w and K_b.[1]

(ii) *Salt of a strong base with a weak acid* (e.g., KCN). By a calculation exactly similar to the above we find:

$$x = -\frac{vK_w}{2K_a} \pm \sqrt{\frac{v^2}{4}\left(\frac{K_w}{K_a}\right)^2 + v\frac{K_w}{K_a}}$$

or, approximately: $x = \sqrt{vK_w/K_a} = \text{const.} \times \sqrt{v}$.

(iii) *Salt of a weak acid and a weak base* (e.g., aniline acetate). The reaction is $AB + H_2O \rightleftharpoons HA + BOH$, the acid and base being practically unionized. With the same notation as before we find (the salt being nearly completely ionized):

$$[AB] = (1-x)/v, \qquad [A'] = (1-x)/v = [B^{\cdot}].$$

Also $[HA] = x/v = [BOH]$. The following three relations hold good:

$$K_w = [H^{\cdot}][OH'],$$

$$K_a = [H^{\cdot}][A']/[HA] = [H^{\cdot}]\frac{1-x}{v}\Big/\frac{x}{v},$$

$$K_b = [B^{\cdot}][OH']/[BOH] = [OH']\frac{1-x}{v}\Big/\frac{x}{v},$$

[1] Cf. Noyes and Melcher, *Carnegie Inst. Pub.*, No. 63, p. 94; hydrolysis of salts of weak bases and strong acids increases with rise of temperature.

from which follows:

$$K_a K_b = K_w[(1 - x)/x]^2.$$

Thus:

$$(1 - x)/x = K_a^{1/2} . K_b^{1/2}/K_w^{1/2} = \text{const.}$$

Hence x, the degree of hydrolysis, is independent of dilution. We have also:[1]

$$[H^+] = K_a x/(1 - x) = K_a K_w^{1/2}/K_a^{1/2} . K_b^{1/2} = \text{const.}$$

The methods used in determining degree of hydrolysis are as follows:

(i) *Measurement of the catalytic effect of the* H^+ *or* OH' *ion*, e.g., in the hydrolysis of an ester or the rate of inversion of cane sugar.[2] The rate of hydrolysis of the ester is determined in presence of a strong acid (or base), and the velocity constant, k, compared with that found when hydrolysis of the ester occurs in presence of the salt.

(ii) *Distribution measurements:* The solution containing the salt is shaken with an immiscible solvent in which the free acid or free base is soluble. From the known distribution ratio, the concentration in the solution is easily calculated.

(iii) *Freezing point lowering.*[3]

(iv) *Conductivity:* Let κ be the observed specific conductivity of a solution of BA of concentration c. The apparent equivalent conductance is $\kappa/c = (1 - x)(\kappa/c)_v + x(\kappa/c)_{HA}$, where κ_v is the conductivity the salt would have possessed had no hydrolysis occurred and κ_{HA} is the conductivity of the acid, assumed strong. The base is assumed very weak, so that it does not enter the conductivity equation. Rewriting the above we get:

$$x = (\Lambda - \Lambda_v)/(\Lambda_{HA} - \Lambda_v).$$

Λ_{HA} is the equivalent conductance of the free acid at practically infinite dilution; Λ_v is found by Bredig's method,[4] which consists in arranging the constituents of the solution so that $\Lambda = \Lambda_v$, i.e., $x = 0$. This is attained by adding excess of the free (practically unionized) base until Λ is constant.[5]

(v) *From values of* K_w, K_a *and* K_b.

(vi) *Determination of* H^+ *concentration by concentration cell measurements.*

Hydrolysis may very appreciably affect the results of conductivity measurements with very dilute solutions, especially when the values of the ionization constants of the acid and base differ.[6]

When the hydrolysis of salts is followed by conductivity, the change some-

[1] Tizard, *J. Chem. Soc.*, **97**, 2490 (1910); hydrolysis of salts occupying intermediate positions, see Rohden, *J. Chim. Phys.*, **13**, 261 (1915); Griffiths, *Trans. Farad. Soc.*, **17**, 525 (1922), has considered the situation in extremely dilute solutions, when the weak acid and base are appreciably ionized.

[2] Ley, *Z. physik. Chem.*, **30**, 193 (1899); Bredig and Fraenkel, *Z. Elektrochem.*, **11**, 525 (1905); Kellogg, *J. Am. Chem. Soc.*, **31**, 403, 886 (1909); Henderson and Kellogg, *ibid.*, **35**, 396 (1913) (neutral salt action).

[3] Göbel, *Z. physik. Chem.*, **89**, 49 (1914).

[4] See p. 527; *Z. physik. Chem.*, **13**, 191 (1894); Ikawa, *Mem. Coll. Sci. Eng. Kyoto*, i, 320 (1908).

[5] Cf. Gibbs, Williams and Galajikian, *Philippine J. Sci.*, **8**, 1 (1913); Noyes, Kato and Sosman, *J. Am. Chem. Soc.*, **32**, 159 (1910); Huff and Name, *Am. J. Sci.*, **45**, 103 (1918).

[6] Böttger, *Z. physik. Chem.*, **46**, 602, 604 (1903); Hägglund, *Arkiv. Kem. Min. Geol.*, **4**, No. 11, p. 1 (1911); Euler and Ugglas, *Z. physik. Chem.*, **68**, 498 (1909); Hägglund, *J. Chim. Phys.*, **10**, 207 (1912).

times occurs slowly. This has been attributed to scarcity of ions;[1] to hydrolysis in stages;[2] to hydrate isomerism (e.g., green and violet chromic chlorides); and to colloid formation,[3] since in the case of substances showing this slow hydrolysis the weak acid or weak base often tends to form colloidal solutions.

Amphoteric Electrolytes: Some substances on ionization give two ions simultaneously, one positive and the other negative, leaving a residual molecule with two equal and opposite charges. This residue is considered as an ion, although its net charge is zero:[4]

$$XMY \rightleftharpoons X^+ + {}^-M^+ + Y^-.$$

Such an ion is called an *amphoteric* ("Zwitter") *ion.* Examples are shown by glycine, *o*-aminobenzoic acid, and perhaps methyl orange:

$$NH_2CH_2COOH + H_2O \rightleftharpoons HO.NH_3.CH_2COOH$$
$$\rightleftharpoons OH' + \overset{+}{N}H_3CH_2C\overset{-}{O}O + H^{\cdot}.$$

Very little is known of such types of equilibrium, although they are perhaps more common than is usually supposed.[5] Although amphoteric ions do not give rise to conductivity their presence is shown by their effect, by reason of their dipole character, on the dielectric constant of the solvent.[6]

Beveridge[7] considers that the degree of hydrolysis of amphoteric electrolytes as determined by conductivity methods differs from that found by catalytic measurements. Methods which depend on $H^{\cdot}$ concentration all agree among themselves, but indirect methods depending on conductivity, freezing point, etc., give different values.

[1] Kovalevski, *Z. anorg. Chem.*, **23**, 1 (1900).

[2] Antony and Giglio, *Gazetta*, **25**, 1 (1895); Goodwin, *Z. physik. Chem.*, **21**, 1 (1896); Malfitano, *Ann. Chim. Phys.*, **25**, 159 (1912); Quartaroli, *Gazetta*, **45**, 139 (1915).

[3] Wagner, *Monatsh.*, **34**, 95 (1913); disputed by Tian, *Compt. rend.*, **172**, 1179 (1921); *J. Chim. Phys.*, **19**, 190 (1921). On the hydrolysis of aluminates see Hantzsch, *Z. anorg. Chem.*, **75**, 371 (1912); **30**, 289; Mahin, Ingraham and Stewart, *J. Am. Chem. Soc.*, **35**, 30 (1913); severely criticized by Blum, *ibid.*, 1499, and Slade and Polack, *Trans. Farad. Soc.*, **10**, 150 (1914); cf. Noyes and Whitney, *Z. physik. Chem.*, **15**, 694 (1894). The reaction is:

$$Al(OH)_3 + OH' = Al(OH)_2O' + H_2O = Al(OH)_2OH + OH';$$

the conductivity increases slowly at first (first stage), then rapidly (second stage), and then slowly (decreasing concentrations). See under "Amphoteric Electrolytes."

[4] Küster, *Z. anorg. Chem.*, **13**, 127 (1896); Winkelblech, *Z. physik. Chem.*, **36**, 546 (1901); Lunden, *Arkiv. Kem. Min. Geol.*, **2**, No. 18, 1 (1906); *Z. physik. Chem.*, **54**, 532 (1906); *Sammulung Chem. u. Chem. tech. Vorträge*, **14**, 49 (1908); Robertson, *J. Phys. Chem.*, **10**, 524 (1906).

[5] Nernst, Lehrbuch, 8–10 Aufl., p. 440; he refers to carbon monoxide as $\underset{+}{C} = O$.

[6] Küster, *Z. anorg. Chem.*, **13**, 136 (1897); Bjerrum, *Z. physik. Chem.*, **104**, 147 (1923); Blüh, *ibid.*, **106**, 341 (1923); **111**, 25 (1924); Thiel and Dassler, *ibid.*, **108**, 298 (1924); Ebert, *ibid.*, **121**, 385 (1926).

[7] *Proc. Roy. Soc. Edinb.*, **29**, 648 (1909).

Adams [1] has considered amphoteric electrolytes from the point of view of the relative strengths of the acidic and basic functions. If we consider the dibasic acid HAH and treat the two $H^{\cdot}$ ions independently, we have:

$$K_1 = [H^{\cdot}][AH']/[HAH]; \qquad K_2 = [H^{\cdot}][HA']/[HAH];$$
$$K_3 = [H^{\cdot}][A'']/[HA']; \qquad K_4 = [H^{\cdot}][A'']/[AH'].$$

If we represent the first and second ionization constants of the acid by K' and K'', respectively, we have:

$$K' = K_1 + K_2; \qquad K'' = K_3K_4/(K_3 + K_4).$$

Three cases arise: (*a*) the acid is symmetrical and the H atoms ionize independently: $K_1 = K_2 = K_3 = K_4 = K$ and $K' = 2K$; $K'' = \frac{1}{2}K$; (*b*) the acid is unsymmetrical but the H atoms ionize independently: $K_3 = K_1$; $K_4 = K_2$ and $K'' = K_1K_2/(K_1 + K_2)$; (*c*) the acid is unsymmetrical and the H atoms do not ionize independently. Then $K'/K'' > 4$. For a tribasic acid, $K'/K'' > 3$. For phenolphthalein and crystal violet, K'/K'' is nearly equal to 4. In the case of glycine K_a (the acidic constant) is 1.8×10^{-10} and K_b (the basic constant) is 2.8×10^{-12}, so that $K' = 3.7 \times 10^{-3}$ and $K'' = 1.8 \times 10^{-10}$. It is nearly as strong a base as methylamine and is a stronger acid than monochloracetic.

Michaelis [2] finds, if x is the proportion of unionized molecules of an amphoteric electrolyte, that:

$$x = 1/(1 + K_a/[H^{\cdot}] + K_b/[OH']),$$

where K_a and K_b are the acidic and basic dissociation constants, respectively. Substances for which $K_aK_b \gtrless 10^{-14}$ are not capable of existing; at this point complete dissociation occurs.

Substances such as lead and aluminium hydroxides are sometimes called amphoteric electrolytes, since they behave as acids towards strong bases and as bases towards strong acids. The dissociation of such substances is really hydrolytic in character, and has already been considered.

Solubility Product: The effect of one substance in influencing the solubility of another is fairly general. The solubility of non-electrolytes in the presence of electrolytes is generally depressed according to the equations:

$$S = S_0(1 - Bc) \text{ or more exactly } S = S_0e^{-Bc},$$

where c is the concentration of electrolyte, and A, B are constants.[3]

[1] *J. Am. Chem. Soc.*, **38**, 1503 (1916); Bjerrum, *Z. physik. Chem.*, **104**, 147 (1923); Ebert, *ibid.*, **121**, 385 (1926); Bork, *ibid.*, **129**, 58 (1927).

[2] *Biochem. Z.*, **33**, 182 (1911).

[3] Rothmund, *Z. Elektrochem.*, **7**, 675 (1901); *Z. physik. Chem.*, **69**, 523 (1909); Nernst, *ibid.*, **38**, 494 (1901); Findlay, *J. Chem. Soc.*, **97**, 536 (1910); **101**, 1459 (1912); Geffeken, *Z. physik. Chem.*, **49**, 257 (1904); Euler, *ibid.*, **49**, 303 (1904); Thorin, *ibid.*, **89**, 685 (1915); Rothmund, Löslichkeit und Löslichkeitsbeeinflussung, Leipzig, 1907; Euler and Svanberg, *Z. Elektrochem.*, **23**, 192 (1917).

The effect is a specific property of the electrolyte, although the order of electrolytes as regards their effect on solubility is nearly the same for different solutes. The effect, sometimes known as "salting out," is not confined to electrolytes: the effect of sugar in reducing the solubility of hydrogen in water is greater than that of salts (Euler, *loc. cit.*).[1] In some cases addition of salt causes a marked increase in the solubility of a non-electrolyte, e.g., salts of aromatic acids in the case of ether and water (Thorin, *loc. cit.*). The solubility of salts is in general depressed, but not always, by addition of non-electrolytes, the solubility change being nearly, but not quite, a linear relation (Rothmund, *loc. cit.*).

The solubilities of electrolytes in presence of each other, especially when a common ion is present, is of more importance than the above cases.

Consider the equilibrium:

$$\text{AgCl (solid)} \rightleftharpoons \text{AgCl (satd. sol.)}.$$

If by any means the amount of dissolved salt is decreased, more solid will pass into solution to maintain saturation. The dissolved salt is ionized:

$$\text{AgCl (solid)} \rightleftharpoons \text{AgCl (dissolved)} \rightleftharpoons \text{Ag}^{\cdot} + \text{Cl}'.$$

If the law of mass action applies:

$$[\text{Ag}^{\cdot}][\text{Cl}']/[\text{AgCl}] = K \qquad \text{or} \qquad [\text{Ag}^{\cdot}][\text{Cl}'] = K[\text{AgCl}].$$

The concentration $[\text{AgCl}]$ is called the *molecular solubility*; it is assumed to be constant at a given temperature, even if other substances are present, and equal to its value in a saturated solution of the pure salt. Hence the term $K[\text{AgCl}]$ is constant. Hence: $[\text{Ag}^{\cdot}][\text{Cl}'] = const. = S$, where S is called the *solubility product* of silver chloride. It may be assumed that this relation holds good when the concentrations $[\text{Ag}^{\cdot}]$ and $[\text{Cl}']$ are not equal, and that solid AgCl is in equilibrium with a solution containing its ions when the *ionic product* $[\text{Ag}^{\cdot}][\text{Cl}']$ is equal to the solubility product. If the salt is completely ionized, which is very nearly the case with AgCl on account of the great dilution, then, if x is the solubility, $S = x^2$, since each ion concentration is equal to x.

If the ionic product exceeds S, solid salt will precipitate out of solution until the ionic product becomes equal to S. This is illustrated by the precipitation of NaCl from a saturated solution by HCl gas. The Cl′ concentration is increased, so that the product $[\text{Na}^{\cdot}][\text{Cl}']$ now exceeds its value in the saturated solution of NaCl. The precipitation restores the value S of $[\text{Na}^{\cdot}] \times [\text{Cl}']$, but this is now the product of a large Cl′ concentration with a small $\text{Na}^{\cdot}$ concentration, the excess of Cl′ being paired with the $\text{H}^{\cdot}$ in the solution.

The quantitative aspect of the solubility product relation was first described by Nernst.[2] Consider a completely ionized binary electrolyte AB dissociated into the ions $A^{\cdot}$ and B'. Then $[A^{\cdot}][B'] = \text{const.} = L_0^2$, where L_0 is the solubility. Suppose now x mols of a second completely ionized electrolyte

[1] Cf. Armstrong, *Proc. Roy. Soc.*, **81**, 80 (1908).]

[2] *Z. physik. Chem.*, **4**, 372 (1889).

with a common ion is added. The solubility of the first salt is reduced to L where $L(L + x) = L_0^2$. This equation holds only for complete ionization of both salts, a condition rarely met with in practice.

Let α_0 be the ionization of the first salt in saturated solution, before any of the second salt is added. Let α_2 be the ionization of the second added salt in the solution, and α_1 the ionization of the first salt when the second is added. The concentrations of the ions of the first salt are $L\alpha_1$ and $L\alpha_1 + x\alpha_2$, where x mols. of the second salt are added. The ionic product is $L\alpha_1(L\alpha_1 + x\alpha_2)$. Assuming this to be equal to the ionic product of the first substance alone in saturated solution, we have:

$$L\alpha_1(L\alpha_1 + x\alpha_2) = L_0^2\alpha_0^2.$$

By solving this equation for L we find:

$$L = -\frac{x\alpha_2}{2\alpha_1} + \sqrt{\frac{x^2\alpha_2^2}{4\alpha_1^2} + \frac{L_0^2\alpha_0^2}{\alpha_1^2}}.$$

If $\alpha_1 = \alpha_2 = \alpha$, this reduces to:

$$L = -\frac{x}{2} + \sqrt{\frac{x^2}{4} + \frac{L_0^2\alpha_0^2}{\alpha^2}}.$$

These equations enable us to calculate the solubility of one salt in presence of a second salt with a common ion.

In estimating the ionizations the rule of Arrhenius [1] is frequently used: in a mixture of two salts with a common ion, each salt has a degree of ionization equal to that which it has when present alone in a solution in which its ions have a concentration equal to the concentration of the common ion in the mixture.

The following scheme of calculation is useful. Let the equilibrium be:

$$AB + CB \rightleftarrows A' + 2B' + C'$$

Known		*Unknown*	
Total solubility of AB in pure water	$= m_0$	Conc. of molecular AB	$= a$
Total conc. of CB added	$= n$	Conc. of molecular CB	$= b$
Dilution constant for CB	$= k_b$	Conc. of A ions	$= A$
Molecular solubility of AB	$= k_a$	Conc. of B ions	$= B$
Solubility product of AB	$= k$	Conc. of C ions	$= C$
		Total solubility of AB	$= m$

There are six unknowns, and six equations may be written down and solved for m:

(1) $m = A + a$,
(2) $m + n = a + b + B$,
(3) $n = C + b$,
(4) $c \times B/b = k_b$ or some other dilution formula with *known* constants (i.e. Storch's),
(5) $a = k_a$,
(6) $A \times B = k$.

Shorter methods of approximation are generally used (Noyes, *loc. cit.*)

[1] *Z. physik. Chem.*, **2**, 284 (1888); **31**, 218 (1899); another rule is that of Barmwater, *Z. physik. Chem.*, **28**, 424 (1899); **45**, 557 (1903); **56**, 225 (1906) in which the ionization is assumed to be equal to that of the salt present alone at a concentration equal to the *total salt*

The experimental results in a few typical cases are represented by the curves in Figs. 18, 19 and 20.[1]

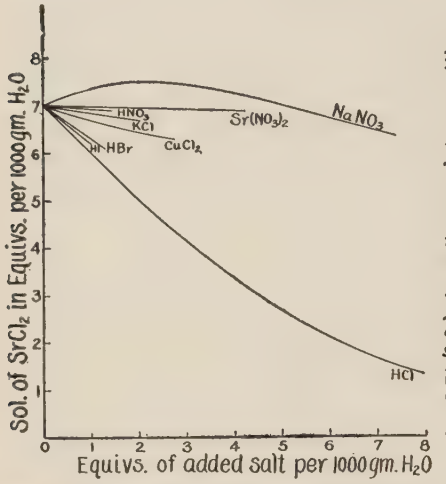

Fig. 18. Solubilities of Strontium Chloride in Presence of Other Salts

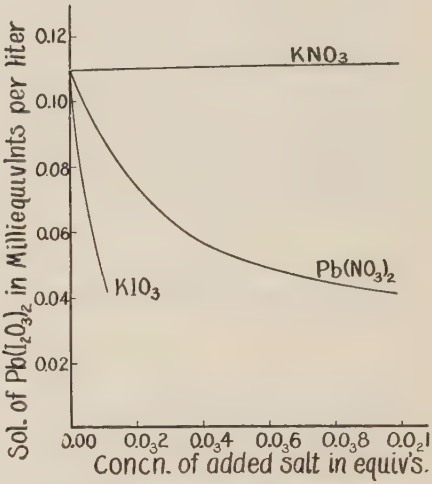

Fig. 19. Solubilities of Lead Iodate in Salt Solutions

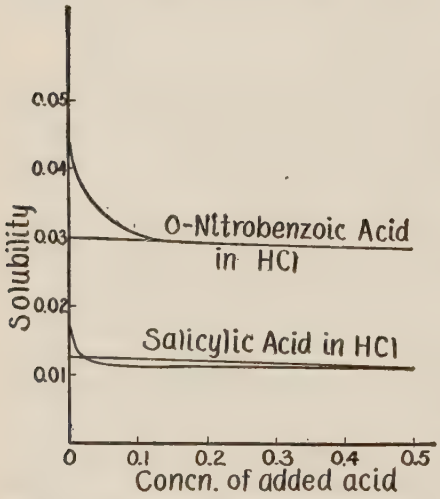

Fig. 20. Solubilities of Acids in Hydrochloric Acid Solutions

In the case of $SrCl_2$ (Fig. 18) it is seen that the effect of substances without a common ion is not great. HCl causes the greatest effect, although HBr and HI, which have no common ion, also cause nearly as great a depression of solubility. $NaNO_3$, without a common ion, at first causes a slight increase in solubility, then a decrease.

The curves for $Pb(IO_3)_2$ are more in accordance with the theory as far as qualitative results go (Fig. 19).

The curves in Fig. 20 relate to the solubilities of moderately strong organic acids in presence of HCl at 25°.[2] There is at first a rapid fall in solubility, as indicated by theory, then a nearly constant, slightly decreasing solubility, is reached on further addition of HCl.

All these results show that the simple theory of solubility product does not adequately represent the facts. The experiments of Nernst (*loc. cit.*) and of Noyes[3]

concentration of the mixture. The results usually do not differ very much from those of Arrhenius' assumption; King and Partington, *Trans. Farad. Soc.*, **23**, 531 (1927); Hawkins and Partington, *ibid.*, **24**, 518 (1928); Partington and Tweedy, "Calculations in Physical Chemistry," 1928, p. 103.

[1] Kraus, Electrically Conducting Systems, pp. 271–272.

[2] *Proc. Roy. Soc.*, **85**, 200 (1911).

[3] *Z. physik. Chem.*, **6**, 241 (1890).

showed better agreement. Noyes worked with silver bromate and nitrate, as well as with thallium salts, $TlNO_3$ with KNO_3, TlCNS with KCNS and $TlNO_3$. The silver salts gave satisfactory results, but the thallium salts did not conform to the theory. Noyes concluded that either the law of solubility product is incorrect, or else that conductivity measurements do not give a correct measure of the ionization. He then reversed the procedure and used solubility measurements to determine the degree of ionization.[1] In this way with $TlNO_3$, a strong electrolyte, he obtained values which agreed with Ostwald's dilution law. Kendall [2] has pointed out that this method may give erroneous results. Other experiments of Noyes [3] with tervalent chlorides also gave results in agreement with Ostwald's formula. The discrepancies were cleared up when Noyes found [4] that TlCl does not ionize to the same extent as alkali chlorides, as had previously been assumed. When this correction was made, the degrees of ionization found by solubility and conductivity methods were in agreement.

More recently the law of constancy of solubility product has been called in question.[5] Cameron found that the solubility of gypsum is increased by the addition of NaCl up to a certain point, but on further addition the solubility is depressed. Hill and Simmons found the same result with silver sulphate and nitric acid. Hill [6] pointed out that these results could only be explained on the assumption that the solubility products of gypsum and silver sulphate are not constant in presence of other electrolytes, and he proved that the same holds in the case of TlCl and Et_4NI, the product decreasing with increasing concentration of total electrolyte present.

Many other irregularities of this kind have been noticed. Thus Bray and Winninghoff [7] found the solubility of TlCl (in water) increased on addition of K_2SO_4 or KNO_3, but decreased in presence of KCl, $BaCl_2$ and Tl_2SO_4.

Kendall [2] experimented with slightly soluble organic acids (salicylic, *o*-nitrobenzoic), in presence of a second acid (picric, HCl) in aqueous solution at 25°. Real divergencies from constant solubility product were found. These were positive or negative according as the acids were chemically similar or dissimilar. The solubility of an acid in a solution of another acid is made up of two parts, one of which increases or decreases regularly according as the acid is more or less soluble in the aqueous second acid than in pure water, whilst the second part of the solubility decreases fairly rapidly according to the ionic strength of the solvent acid. All observed divergencies from constant solubility product can be satisfactorily explained by the first of these causes. Noyes' proposed method of determining ionization on the basis of the solubility method cannot therefore lead to accurate results.

Experiments of Hill [8] with $AgBrO_3$, TlCl and $PbCl_2$ in presence of varying amounts of acetic acid indicated that the solubility product decreases with increase in concentration of the more soluble electrolyte. Hill interprets his results as follows. Suppose the solution is saturated with AB and the added electrolyte is CD. The mixed solution contains the salts AB, CD, AD, and CB and the ions $A^{\cdot}$, B', $C^{\cdot}$, D'.[9] The solubility of $AB = L$ is then $[A^{\cdot}] + [AD] = [B'] + [CD]$, from which by multiplication we find $L = \sqrt{AB} + M$, where M has some positive value. It follows that if L becomes less than $\sqrt{AB}$ the solubility product is smaller than it would be in a saturated solution of AB in pure water. Hill's results show that this is the case, except in one instance, the solutility of Me_4NI in aqueous ammonia.

[1] *Z. physik. Chem.*, **6**, 259 (1890).

[2] *Proc. Roy. Soc.*, **85**, 200 (1911).

[3] *Z. physik. Chem.*, **9**, 603 (1892); Bray and Winninghoff, *J. Am. Chem. Soc.*, **33**, 1663 (1911).

[4] *Z. physik. Chem.*, **16**, 125 (1895); **26**, 152 (1898).

[5] Cameron, *J. Phys. Chem.*, **5**, 556 (1901); Hill and Simmons, *J. Am. Chem. Soc.*, **31**, 821 (1909); Brönsted, *J. Am. Chem. Soc.*, **42**, 761, 1448 (1920); *K. Danske Vidensk. Medd. Math. Phys.*, **2**, No. 10, 1 (1919); *J. Chem. Soc.*, **119**, 574 (1921).

[6] *J. Am. Chem. Soc.*, **32**, 1186 (1910).

[7] *J. Am. Chem. Soc.*, **33**, 1671 (1911).

[8] *J. Am. Chem. Soc.*, **39**, 218 (1917).

[9] Complex ions might also be present.

In the case of uni-bivalent salts such as $PbCl_2$, $Ca(OH)_2$, Ag_2SO_4, etc., Noyes and Bray [1] have shown that the solubility product principle breaks down completely. The product increases greatly in such cases, since the addition of the bivalent ion causes no great decrease in concentration of the univalent ion of the salt with which the solution is saturated. The conception of solubility product is "an approximate empirical principle" without theoretical foundation, according to Stieglitz.[2] The principle of the constancy of molecular concentration, i.e., concentration of unionized molecules, $[AB] = const.$ in presence of ions has also been disproved experimentally. Although an ion concentration, say $[A^{\cdot}]$, may be depressed almost to zero by addition of a salt with a common ion, the total solubility of the salt should never be less than the molecular solubility. Arrhenius [3] showed from some results of Noyes that in the case of silver salts the total solubility had been depressed below the value of the molecular solubility. This occurred, it is true, only when large amounts of added salt were present, and the approximate constancy of the molecular solubility may be assumd when the concentration of added salt is not large.

Better agreement has been obtained when a soluble salt has been added to a saturated solution of a sparingly soluble salt so that another sparingly soluble salt is produced.[4] For example:

$$TlCl + KCNS \rightleftharpoons TlCNS + KCl$$

the TlCl and TlCNS being sparingly soluble. Since these two salts are practically completely ionized we have:

$$[Tl^{\cdot}][Cl'] = L_1^2,$$
$$[Tl^{\cdot}][CNS'] = L_2^2,$$

where L_1, L_2 are the solubilities of TlCl and TlCNS. Hence

$$[Cl']/[CNS'] = L_1^2/L_2^2,$$

showing that the ratio of the concentrations of the ions not common to both salts is the ratio of the squares of the solubilities of the two salts. In this way the concentrations of ions which can be in equilibrium with two such salts may be calculated from the solubilities, or, conversely, the relative solubilities may be calculated if the ratio of ion concentrations has been found by experiment. The results in several cases were satisfactory.

Bray [5] has attempted to find a fresh theoretical basis for the law of solubility. The solubilities of ternary and higher types of salts have been investigated by Harkins,[6] but the results are not easily interpreted. Working with solutions of KCl, $Ba(BrO_3)_2$ and $PbCl_2$, he found:

(i) Addition of a salt of common univalent ion causes rapid decrease in solubility (in accordance with the solubility-product principle).

(ii) Addition of a salt containing a common bivalent ion causes:
- (*a*) Slight decrease and then increase in the solubility of the salt if the latter is moderately soluble;
- (*b*) Slight but continuous decrease in the solubility of less soluble salts (this was only confirmed to a concentration 0.2 n. of the added salt);
- (*c*) Continuous increase in solubility in the case of extremely soluble salts.

(iii) Addition of a salt with no common ion causes increase in solubility.

[1] *J. Am. Chem. Soc.*, **33**, 1643 (1911); Noyes, Boggs, Farrell and Stewart, *ibid.*, p. 1650.

[2] *J. Am. Chem. Soc.*, **30**, 946 (1908); cf. Findlay, *Z. physik. Chem.*, **34**, 409 (1900).

[3] *Z. physik. Chem.*, **31**, 197 (1899).

[4] Knüppfer, *Z. physik. Chem.*, **26**, 255 (1898); Findlay, *ibid.*, **34**, 407 (1900); Foote, *ibid.*, **33**, 740 (1900); Noyes and Kohr, *ibid.*, **42**, 336 (1902); *J. Am. Chem. Soc.*, **24**, 1141 (1902); Foote and Menge, *Am. Chem. J.*, **35**, 432 (1906); Hill, *J. Am. Chem. Soc.*, **30**, 68 (1908).

[5] *J. Am. Chem. Soc.*, **33**, 1673 (1911).

[6] *J. Am. Chem. Soc.*, **33**, 1807 (1911); Harkins and Pearce, *ibid.*, **38**, 2679, 2709, 2714 (1916).

The interpretation of experimental results is somewhat uncertain because the ionization functions of each of the mixed electrolytes are unknown. In the cases of higher electrolytes especially, intermediate ions may exert an unknown effect and Harkins has shown that the solubility curves of these electrolytes may be qualitatively explained if the presence of such ions is assumed. Kendall and Andrews [1] measured the solubilities of acids of varying strength.

The case of the effect of one salt on the solubility of another with which it has no ion in common has been studied by Noyes.[2] Let AB be sparingly soluble, then in consequence of the equilibrium:

$$AB + CD \rightleftharpoons AD + CB$$

the solubility of AB will be increased and the increase will be greater when the products of reaction (or one of them) are ionized only to small extents. Experiments on the solubility of a salt of a weak acid (e.g., silver benzoate) in a solution of a strong acid (e.g., nitric acid) gave results in fairly good agreement with the calculated values. In the solution there are four kinds of ions and four kinds of undissociated molecules, the concentrations of which, and the total solubility of AB, L, make nine unknowns. There will be four simple linear equations expressing the result that the total concentration of any one salt is equal to the sum of the concentrations of the undisssociated part and those of the ions; three equations expressing the equilibrium relations between undissociated part and ions for the three salts CD, AD, and CB; and two equations expressing the constancy of the solubility product $[A^{\cdot}][B']$, and the constancy of the molecular solubility of AB, respectively. Thus L may be calculated from the nine equations.

Complex Ions [3]

In some cases the solubility of a sparingly soluble substance is considerably greater in a solution of a salt with a common ion than in pure water. For example, silver cyanide is readily soluble in a solution of potassium cyanide. In such cases *complex ions* are usually formed, with which only very small amounts of the simple ion are in equilibrium:

[1] *J. Am. Chem. Soc.*, **43**, 1545 (1921).

[2] *Z. physik. Chem.*, **27**, 267 (1898); Noyes and Schwartz, *ibid.*, **27**, 279 (1898); *J. Am. Chem. Soc.*, **20**, 742 (1898); Noyes and Chapin, *ibid.*, **20**, 751 (1898).

[3] See Complex Ions, A. Jaques, London, 1914; Ostwald, *Z. physik. Chem.*, **3**, 596 (1889); LeBlanc and Noyes, *ibid.*, **6**, 385 (1890); Reisenfeld and Feld, *Z. Elektrochem.*, **26**, 286 (1920); Stieglitz, *J. Am. Chem. Soc.*, **30**, 946 (1908); Abegg and Bodländer, *Z. anorg. Chem.*, **20**, 471 (1899); Bodländer and Storbeck, *ibid.*, **31**, 475 (1902); Bodländer and Eberlein, *ibid.*, **39**, 197 (1904); Drucker, *Z. Elektrochem.*, **18**, 562 (1912); **19**, 8, 797 (1913); *Z. physik. Chem.*, **96**, 381 (1920); Drucker and Riethof, *ibid.*, **111**, 1 (1924); Drucker and Schingnitz, *ibid.*, **122**, 149 (1926); Sherill, *Z. physik. Chem.*, **43**, 705 (1903); Pick, *Diss., Breslau*, 1906; *Z. anorg. Chem.*, **51**, 1 (1906); W. K. Lewis, *Diss., Breslau*, 1908; Roloff, *Z. physik. Chem.*, **13**, 341 (1894); Jakowkin, *ibid.*, **13**, 539 (1894); **18**, 585 (1895); Plotnikov and Rokotjan, *J. Russ. Phys. Chem. Soc.*, **47**, 723 (1915); Leslie, *J. Chem. Soc.*, **99**, 1601 (1911); see also under the respective metals in Abegg's Anorganische Chemie.

$$AgCN + CN' \rightleftharpoons [Ag(CN)_2]',$$
$$[Ag(CN)_2]' \rightleftharpoons Ag^{\cdot} + 2CN'.$$

The ratio $K = [Ag(CN_2)]'/[AgCN][CN']$ is called the *complex constant.*

Many methods are available for the detection and estimation of complex ions in solutions: purely chemical, migration data, partition coefficients, solubility measurements and application of Nernst's solubility product equation; electrode potentials, and cryoscopic measurements.

Non-Aqueous Solutions

Conductivities of Pure Liquids: The conductivities of pure liquids (including water) are very small, and are very largely influenced by the presence of small traces of impurities, so that their determination is a matter of considerable difficulty.[1]

In some cases, e.g., with sulphur dioxide, ammonia, ether and some hydrocarbons, the results resemble those obtained with gases, so that it has been assumed that these substances have no measurable conductance in the perfectly pure state. The existence of a limiting conductivity which is independent of the intensity does not prove that the liquid is perfectly pure. Carvallo (*loc. cit.*) showed that liquids containing known traces of impurities showed the effect. Previous electrical treatment usually influences the conductivity, methyl alcohol being exceptions. The prolonged passage of current leads to a conductivity limit, which may be greater or less than the true conductivity (Carvallo).[2]

The measurements of Jaffé,[3] made with very pure liquids, showed that, in the case of hexane, the conductivity had a limiting value which was independent of temperature but depended on the nature of the containing vessel. Above 200 volts/cm. the current was independent of the potential gradient, analogous to the saturation current in ionized gases and the results indicated a conductivity due to ionization by radiations from the vessel, as with gases. Part of the ionization was due to external radiation, since the conductivity decreased when the vessel was surrounded by lead screens. The conductivity of hexane when exposed to rays from radium [4] did not agree with the results of Thomson with gases. The specific velocities of the positive and negative ions were 6.03×10^{-4} and 4.17×10^{-4} cm./sec., respectively, and the coefficients of diffusion 1.50×10^{-5} and 1.03×10^{-5}. Van der Bijl,[5] by a method elimi-

[1] Walden, *Z. physik. Chem.*, **46**, 103 (1903); Carvallo, *Compt. rend.*, **151**, 717 (1910); **155**, 1609 (1912); **153**, 1144 (1911); **156**, 1755 (1913); *Ann. Physique*, **1**, 171 (1914); **2**, 142 (1914); Fassbinder, *Ann. Phys.*, **48**, 449 (1915) (considers previous measurements all affected by impurities); Schröder, *ibid.*, **29**, 125 (1909) (physical condition of electrodes affects results); Kraus, Properties of Electrically Conducting Systems, 1922; Walden, Elektrochemie nichtwässriger Lösungen, 1924 (full bibliography); Rabinovitsch, *Z. physik. Chem.*, **119**, 59, 70, 79, 307 (1926).

[2] Cf. H. B. Baker, J. Chem. Soc., 1928, p. 1051.

[3] *Ann. Physik*, **28**, 326 (1909).

[4] Jaffé, *Ann. Physik*, **32**, 148 (1910); cf. Curie, *Compt. rend.*, **134**, 420 (1902).

[5] *Ann. Physik*, **39**, 170 (1912); Bialobjeski, *Le Radium*, **8**, 293 (1911).

nating ionic diffusion, showed that, in the case of hexane, carbon tetrachloride and carbon disulphide, Thomson's formula:

$$du/dt = -an^2$$

is obeyed, n being the number of positive or negative ions per cc. and a the coefficient of combination.[1] It appears, on the whole, as if the conductivities of pure liquids, other than water or ionizing liquids, are similar to those of gases in the mechanism by which the current is carried. As an example of the difficulties met with in this field, reference may be made to the decomposition of liquid sulphur dioxide by light, with formation of products which dissolve and increase the conductivity:[2]

$$3SO_2 = S + 2SO_3.$$

The values of the specific conductance, κ, for pure liquids are given in Table XIII.

TABLE XIII

Conductivities of Liquids at Room Temperature. Values of κ

H_2SO_4	1×10^{-2}	Acetone	0.3×10^{-7}
HNO_3	1.5×10^{-2}	Ammonia	1×10^{-7}
Formic Acid	1.5×10^{-5}	Sulphur Dioxide	$<0.5\times10^{-7}$
Methyl Alcohol	1×10^{-6}	Pyridine	$<0.5\times10^{-7}$
Ethyl Alcohol	1.35×10^{-9}	Chloroform	$<1\times10^{-8}$
Acetonitrile	2×10^{-7}	Benzene	$<1\times10^{-8}$
Nitrobenzene	0.2×10^{-7}	Acetic Acid	2.4×10^{-8}
Benzonitrile	0.5×10^{-7}	Formamide	2.8×10^{-6}

Ionizing Power of Solvents: Dutoit and Aston[3] considered that only associated solvents were capable of ionizing dissolved electrolytes, but the results of Walden[4] show that all liquids are capable of causing ionization to some extent.

One property of the solvent which has a marked influence on its ionizing power is the dielectric constant. This is considered in a later section, but it may be noted that the mass action constant K of an electrolyte decreases rapidly with D, especially when D is less than 10.

The effect of association has also been studied by Turner,[5] who states that all associated liquids are conductors, and the best conductors are those which are most associated. A notable exception is water, and it is doubtful if this rule is general. The constitution of the solvent plays a part; acids in some solvents (e.g., water, alcohols) appear to form complexes with the solvent which are active in carrying the current, solutions in other solvents (e.g., nitrobenzene) having very low conductivities.[6] The chief factor governing the

[1] Conduction of Electricity through Gases, Cambridge, 1906, pp. 16, 17.
[2] Coehn and Becker, *Z. physik. Chem.*, **70**, 88 (1910).
[3] *Compt. rend.*, **125**, 240 (1897).
[4] *Z. physik. Chem.*, **54**, 129 (1906).
[5] *J. Chem. Soc.*, **99**, 880 (1911); Molecular Association, London, 1915.
[6] Kendall and Gross, *J. Am. Chem. Soc.*, **43**, 1426 (1921).

ionizing power of solvents of low dielectric constant is the chemical nature.[1] A close relation between conductivity and specific refraction has been pointed out.[2] This is not remarkable in view of the well-known relation between refraction and dielectric constant.

Determination of Conductance: The general methods used for non-aqueous solutions are the same as those previously described for aqueous solutions. In general, however, much more care is needed to obtain reliable results with non-aqueous solutions than is required with aqueous solutions when the same degree of accuracy is sought. One of the main sources of error is chemical change of the solvent. Thus, alcoholic solutions readily undergo oxidation in contact with platinized electrodes, and the conductance steadily changes if this is not avoided.[3]

The design of conductivity cells has been considered by Morgan and Lammert, on the basis of Washburn's investigations (see p. 517). They have pointed out the modifications required with non-aqueous solutions.[4] The most suitable standard liquid for the determination of the cell constant was found to be standard potassium chloride solution diluted with 95 per cent alcohol instead of water, the solution being forced into the cell by purified air. The usual methods of cleaning and drying the electrodes are inapplicable. A method is described in which the electrodes are kept short-circuited, and the two electrodes should have as nearly as possible the same contact potential when immersed in the solution. When the electrodes are properly cleaned no change of conductivity occurs with change of P.D. Fig. 21 shows a cell designed by Morgan and Lammert (*loc. cit.*) for non-aqueous solutions.[5]

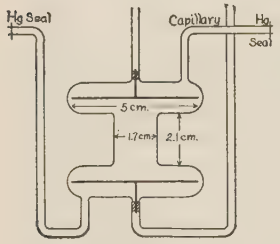

FIG. 21. Conductivity Cell for Non-Aqueous Solutions

Investigations on Non-Aqueous Solutions:[6] The investigations on non-aqueous solutions are of very unequal merit. Some are very inaccurate, and before using any data in this field a very careful comparison is required. Of the earlier results, those of Völlmer[7] may be mentioned as reliable.

The simple relations between conductance and concentration found with aqueous solutions do not, in general, appear when other solvents are used.

[1] Sachanoff, *J. Russ. Phys. Chem. Soc.*, **43**, 526 (1911); *C. A.*, **6**, 179 (1912); Plotnikoff, *Chem. Soc. Abs.*, **114**, (ii), 183 (1918).

[2] Getman and Gibbons, *J. Am. Chem. Soc.*, **37**, 1990 (1915); Walden, *Z. physik. Chem.*, **59**, 385 (1907).

[3] Partington, *J. Chem. Soc.*, **99**, 1938 (1911).

[4] *J. Am. Chem. Soc.*, **45**, 1692 (1923); **46**, 1117 (1924).

[5] Cf. Robertson and Acree, *J. Phys. Chem.*, **19**, 381 (1915); for ordinary work Partington (*loc. cit.*) found the stoppered type of cell, Fig. 2, p. 516, most suitable. The cell is nearly completely filled, and air and moisture excluded by a good stopper covered with Faraday's cement.

[6] Cf. Müller, *Ahrens. Sammlung*, **27**, 268 (1923).

[7] *Ann. Physik*, **52**, 328 (1894).

In some cases, when the dielectric constant is high, the conductance (molar or equivalent) decreases with increasing concentration as in the case of aqueous solutions. This is found with solutions in liquid ammonia and methylamine. In other cases, when the dielectric constant is fairly low (not greater than 20), a minimum conductance may be attained. When the dielectric constant is about 20, the conductance decreases with increasing concentration at low concentrations and becomes constant at higher concentrations.[1] When the solvent has a very low dielectric constant, the conductance increases with the concentration. In all cases, above concentrations of 1 molar, the conductance appears to decrease with increasing concentration.[2]

Steele, McIntosh and Archibald[3] attempted to explain the abnormal results on the assumption of complex formation between solute and solvent, on the basis of which they arrived at the relation

$$\kappa V^n = \alpha K,$$

where κ = specific conductance, α = degree of ionization, V = dilution, K = constant, and n = number of mols. of solute entering into combination. This work has been very severely criticized by Plotnikoff,[4] who shows that it is incapable of covering some known results.

Walden[5] considers that the position of the minimum molar conductance is related to the dielectric constant D of the solvent according to the expression $DV^{1/3}$ = const., for a given electrolyte, where V is the dilution corresponding with the minimum molar conductance (corrected for viscosity).

Creighton and Way state that the value of Λ_∞ is greater in aliphatic than in aromatic solvents of the same type.[6] In the case of *p*-tolyltrimethylammonium iodide the value of Λ_∞ in different solvents is greatest when the latter contain a — CHO group, and least when they contain a — COOH group.

In the case of alcohols[7] the results are more or less similar to those with water; methyl alcohol shows the closest similarity, and the divergence increases with the complexity of the alkyl group, as is shown in the following table of values of Λ_∞ at 25° taken from the results of Goldschmidt and co-workers.[7]

[1] Guerasimov, *J. Russ. Phys. Chem. Soc.*, **58**, 197 (1926); *C. A. Brit.*, **1927**, 113.

[2] Anderson, *J. Phys. Chem.*, **19**, 753 (1915); Mathews and Johnson, *ibid.*, **21**, 294 (1917); Izbekoff and Plotnikoff, *Z. anorg. Chem.*, **71**, 328 (1911); Sachanoff, *Z. physik. Chem.*, **83**, 129 (1913); Sachanoff, *J. Russ. Phys. Chem. Soc.*, **44**, 324 (1912); *C. A.*, **6**, 1564 (1912); Getman and Gibbons, *J. Am. Chem. Soc.*, **36**, 1630 (1914); **37**, 1990 (1915).

[3] Steele and McIntosh, *Proc. Roy. Soc.*, **74**, 321 (1905); Archibald, *J. Am. Chem. Soc.*, **29**, 665 (1907).

[4] *J. Russ. Phys. Chem. Soc.*, **40**, 1243 (1908); *Chem. Soc. Abs.*, **96**, (ii), 13 (1909); Franklin and Gibbs, *J. Am. Chem. Soc.*, **29**, 1389 (1907); see, however, Sachanoff, *J. Russ. Phys. Chem. Soc.*, **43**, 534 (1911); *C. A.*, **6**, 180 (1912); *Z. Elektrochem.*, **19**, 588 (1913); **20**, 529 (1914); *J. Phys. Chem.*, **21**, 169 (1917); Walden, *Z. physik. Chem.*, **100**, 512 (1922).

[5] *Bull. Acad. Sci. Petersburg*, **7**, 1083 (1913); Sachanoff and Prsheborovski, *J. Russ. Phys. Chem. Soc.*, **47**, 849 (1915); Sachanoff and Rabinovitsch, *ibid.*, p. 859; *C. A.*, **9**, 3009 (1915).

[6] *J. Franklin Inst.*, **186**, 675 (1918).

[7] Cattaneo, *R. Acad. Torino*, **28**, 617 (1893); Völlmer, *Ann. Physik*, **52**, 328 (1894); Partington, *J. Chem. Soc.*, **99**, 1937 (1911); *Trans. Farad. Soc.*, **15**, 114 (1919); Robertson

The ionization is smaller than in water,[1] and conductance usually increases with dilution. Similar results have been obtained with solutions in phenol,[2] which is of the water type.

TABLE XIV

	HCl	HBr	HI
Methyl	204	207	212
Ethyl	89	89	93
Propyl	46	47	>HBr
n-Butyl	29	29	>HBr
iso-Butyl	12	15	>HBr

(The values for iso-butyl alcohol are for a dilution of 640 litres; Λ_∞ for HCl is about 19)

Numerous measurements in anhydrous formic acid have been made. The electrolysis of sodium formate in formic acid yields carbon monoxide.[3] The conductances have been determined by Schlesinger and co-workers.[4] Higher fatty acids have also been used. The conductance in acetic acid [5] decreases with dilution, the effect being more rapid with propionic acid. The effects are very marked with concentrated solutions, and complex formation is indicated.[6]

and Acree, *Eighth Internat. Congress Appl. Chem.*, **26**, 609 (1912); *J. Phys. Chem.*, **19**, 381 (1915); Goldschmidt and coworkers, *Z. physik. Chem.*, **89**, 129 (1915); **91**, 46 (1916); *Z. Elektrochem.*, **20**, 473 (1914); Getman and Gibbons, *J. Am. Chem. Soc.*, **37**, 1990 (1915); Kreider and Jones, *Am. Chem. J.*, **45**, 282 (1911); **46**, 574 (1911), and numerous papers by Jones in later issues; Turner, *J. Am. Chem. Soc.*, **40**, 558 (1908); Lloyd and Padree, *Carnegie Inst. Pub.*, **260**, 99 (1918); Dutoit and Rappeport, *J. Chim. Phys.*, **6**, 545 (1908); Archibald and Patrick, *J. Am. Chem. Soc.*, **34**, 369 (1912); methyl alcohol: Völlmer, *loc. cit.;* Kreider and Jones, *loc. cit.;* Goldschmidt and Thuesen, *Z. physik. Chem.*, **81**, 30 (1913); Rimbach and Weitzel, *Z. physik. Chem.*, **79**, 279 (1912); cf. Partington and Grant, *Trans. Farad. Soc.*, **19**, 414 (1923); Walden, Ulich and Laŭn, *Z. physik. Chem.*, **114**, 275 (1924); Walden and Ulich, *ibid.*, p. 297; Goldschmidt and Aarflot, *Z. physik. Chem.*, **117**, 312 (1925); **119**, 1 (1926); Goldschmidt and Mathiesen, *ibid.*, **121**, 153 (1926); Goldschmidt and Dahl, *ibid.*, **114**, 1 (1925); Goldschmidt and others, *ibid.*, **124**, 23 (1926); Goldschmidt and Thomas, *ibid.*, **126**, 24 (1927); Michaelis and Mitzutani, *ibid.*, **116**, 135 (1925); Mitzutani, *ibid.*, **116**, 350 (1925); **118**, 327 (1925); Goldschmidt, Marŭm and Thomas, *ibid.*, **129**, 223 (1927); *ibid.*, **132**, 257 (1928); Tschugajeff and Vladimiroff, *Z. anorg. Chem.*, **135**, 392 (1924); Frazer and Hartley, *Proc. Roy. Soc.*, **109**, 351 (1925).

[1] Keyes and Winninghoff, *J. Am. Chem. Soc.*, **38**, 1178 (1916); Bishop and Kraus, *ibid.*, **43**, 1568 (1921); **44**, 2206 (1922).

[2] Kraus and Kurtz, *J. Am. Chem. Soc.*, **44**, 2464 (1922).

[3] Hopfgartner, *Monatsh.*, **32**, 523 (1911).

[4] *J. Am. Chem. Soc.*, **36**, 1589 (1914); **38**, 271 (1916); **41**, 72, 1921 (1919).

[5] Sachanoff, *J. Russ. Phys. Chem. Soc.*, **43**, 526 (1911); Stranathan and Strong, *J. Phys. Chem.*, **31**, 1420 (1927).

[6] Sachanoff, *J. Russ. Phys. Chem. Soc.*, **43**, 534 (1911); *C. A.*, **6**, 180 (1912); Hopfgartner, *Monatsh.*, **33**, 123 (1912); **34**, 1313 (1913); Konovaloff, *J. Russ. Phys. Chem. Soc.*, **24**, 440 (1893); *Chem. Soc. Abs.*, **64**, (ii), 356 (1893).

Amines have been investigated by Sachanoff,[1] who found that the conductances in aniline, methylaniline, and dimethylaniline decrease in the order given. Dimethylaniline is on the border between ionizing and non-ionizing solvents. Aliphatic amines[2] and pyridine[3] have been investigated. In nitrobenzene solutions halogens are non-conductors[4] whilst ICl_3, IBr give conducting solutions, electrolysis of which takes place according to Faraday's law.[5]

A very interesting solvent is formamide, $H.CO.NH_2$, which forms good conducting solutions, although less so than water. The physical properties of the two solvents are very similar. In some cases the results are different, e.g., CBr_3COOH is highly ionized in water but only slightly so in formamide.[6]

An extensive series of measurements have been made in anhydrous ammonia.[7] The solutions behave similarly to aqueous solutions in that the conductance increases with dilution and attains a limiting value.[8] The conductance of a salt in ammonia is, in general, higher than that in water, although the ionization is less. Ammonia approaches alcohol and acetone in ionizing power. In some cases (e.g., KNH_2, $HgCy_2$ and AgCN) a minimum conductance is observed. Franklin[9] found in the case of $Cu(NO_3)_2$, $Zn(NO_3)_2$, $KHgCy_2$ and KNH_2 two maxima and a minimum. Solutions of alkali metals in ammonia at the boiling point ($-33.5°$) conduct ionically, the negative ions being free electrons.[10] Concentrated solutions exhibit metallic conductance, and at the highest concentrations resemble alloys. The value of κ for saturated solutions of K and Na is of the same order as that for metallic iron.[11] On dilution, the conductivity falls rapidly.

[1] *J. Russ. Phys. Chem. Soc.*, **42**, 683 (1910); *C. A.*, **5**, 3749 (1911); **44**, 324 (1912); *C. A.*, **45**, 102 (1913); *C. A.*, **7**, 1831 (1913); *Z. physik. Chem.*, **85**, 129 (1913); Pound, *J. Phys. Chem.*, **31**, 547 (1927).

[2] Fitzgerald, *J. Phys. Chem.*, **16**, 621 (1912).

[3] Baskov, *J. Russ. Phys. Chem. Soc.*, **46**, 1699 (1914); *C. A.*, **9**, 2171 (1915); Anderson, *J. Phys. Chem.*, **19**, 753 (1915); Mathews and Johnson, *ibid.*, **21**, 294 (1917). Pyridine is used as solvent in preparing some metals, e.g., Li, by electrolysis.

[4] Bruner, *Z. Elektrochem.*, **16**, 204 (1910); *Bull. Acad. Sci. Cracov.*, 731 (1907); cf. Finkelstein and Kudra, *Z. physik. Chem.*, **131**, 338 (1928); Plotnikow and Bendetzky, *ibid.*, **124**, 225 (1927).

[5] Bruner and Galecki, *Z. physik. Chem.*, **84**, 513 (1913); ICl_3 solutions in acetic acid, Brŭns, *ibid.*, **118** ,89 (1925).

[6] Röhler, *Z. Elektrochem.*, **16**, 419 (1910); Walden, *Bull. Acad. Sci. Petersb.*, **5**, 1055 (1911); Davis and Johnson, *Carnegie Inst. Pub.*, **260**, 71 (1918); Jones, Davis and Putnam, *J. Franklin Inst.*, **180**, 567 (1915); other organic solvents, Walden, *loc. cit.*, **7**, 559, 907 (1913).

[7] See Kraus, Electrically Conducting Systems, 1922.

[8] Franklin and Kraus, *Am. Chem. J.*, **23**, 277 (1900).

[9] *Z. physik. Chem.*, **69**, 272 (1909); cf. Franklin and Gibbs, *J. Am. Chem. Soc.*, **29**, 1389 (1907) (methylamine).

[10] Kraus, *J. Am. Chem. Soc.*, **30**, 653, 1197, 1323 (1908); **36**, 864 (1914); **43**, 749 (1921); Gibson and Phipps, *ibid.*, **48**, 312 (1925)—also in CH_3NH_2.

[11] Kraus and Lucasse, *J. Am. Chem. Soc.*, **43**, 2529 (1921); *ibid.*, **44**, 1941 (1922); **45**, 2551 (1923).

Liquid halogens,[1] halogen hydracids,[2] glycerol,[3] benzene,[4] chloroform,[5] hydrogen peroxide,[6] sulphur dioxide,[7] aluminium bromide,[8] sulphuric acid,[9] hydrocyanic acid,[10] acetamide,[11] metal alkyls,[12] acetone,[13] nitromethane,[14] acetonitrile,[15] ether,[16] benzonitrile,[17] and other non-aqueous solvents have been examined. The classical researches are those of Walden,[18] who examined a large number of substances (PCl_3, $POCl_3$, PBr_3, $AsBr_3$, SO_2, SO_3, $SOCl_2$, SO_2Cl_2, S_2Cl_2, H_2SO_4, $SbCl_3$, $SbCl_5$, BCl_3, $SiCl_4$, $SnCl_4$, Br_2, $SO_2(OH)Cl$, $SO_2(OCH_3)_2$, organic solvents) and gives extensive references to the literature.

Svedberg[19] finds that the temperature coefficient of conductivity in anisotropic solvents is abnormally high; a sharp change in conductivity occurs at the transition point.

Temperature Coefficient of Conductivity in Non-Aqueous Solutions: The conductivity of many salts in organic solvents increases with temperature.[20]

[1] Plotnikoff, *J. Russ. Phys. Chem. Soc.*, **49**, 76 (1917); Plotnikoff and Rokotjan, *ibid.*, **45**, 193 (1913); *C. A.*, **7**, 2148 (1913); Johnson and McIntosh. *J. Am. Chem. Soc.*, **31**, 1138 (1909); Mennie and McIntosh, *Trans. Roy. Soc. Canada*, **16**, iii, 301 (1922); Walden, see below; Bruno, *Z. anorg. Chem.*, **163**, 120 (1927).

[2] Archibald, *J. Am. Chem. Soc.*, **34**, 584 (1912); **29**, 665, 1416 (1907).

[3] Guy and Jones, *Am. Chem. J.*, **46**, 131 (1911).

[4] Allen, *Kansas Univ. Sci. Bull.*, 1905; Cady and Lichtenwalter, *J. Am. Chem. Soc.*, **35**, 1434 (1913); Koenig, *ibid.*, **36**, 951 (1914); Cady and Baldwin, *ibid.*, **43**, 646 (1921) (benzene solutions of dry salts have a real conductivity); Jakubsohn, *Z. physik. Chem.*, **118**, 31 (1925); Rabinovitsch, *ibid.*, **132**, 83 (1928).

[5] Walden, *Bull. Acad. Sci. Petersb.*, **7**, 907 (1913); also CCl_4; *Z. anorg. Chem.*, **115**, 49 (1921) (summary of results for organic solvents).

[6] Jones and Murray, *Am. Chem. J.*, **30**, 205 (1903) (sulphuric and acetic acids more strongly ionized than in water).

[7] Walden; Dutoit and Gyr, *J. Chim. Phys.*, **7**, 189 (1909); Franklin, *J. Phys. Chem.*, **15**, 675 (1911).

[8] Izbekoff and Plotnikoff, *J. Russ. Phys. Chem. Soc.*, **43**, 18 (1911); *Z. anorg. Chem.*, **71**, 328 (1911).

[9] Kendall, Adler and Davidson, *J. Am. Chem. Soc.*, **43**, 1846 (1921).

[10] Kahlenberg and Schlundt, *J. Phys. Chem.*, **6**, 447 (1902).

[11] Belladen, *Gazz.*, **57**, 407, 412 (1927).

[12] Hein, Petzchner, Wagner and Segitz, *Z. anorg. Chem.*, **141**, 161 (1925).

[13] Walden, *Z. physik. Chem.*, **54**, 208 (1906); Dutoit and Levier, *J. Chim. Phys.*, **3**, 435 (1905); Brownson and Cray, *J. Chem. Soc.*, **127**, 2923 (1925); Roshdestwensky, *ibid.*, **99**, 2138 (1911).

[14] Philip and Oakley, *J. Chem. Soc.*, **125**, 1189 (1924).

[15] Koch, *J. Chem. Soc.*, 1927, p. 647.

[16] Ussanovitch, *Z. physik. Chem.*, **124**, 427 (1926).

[17] Walden, *Z. physik. Chem.*, **54**, 189; **55**, 710 (1906); Dutoit, *Z. Elektrochem.*, **12**, 643 (1906); Martin, *J. Chem. Soc.*, 1928, 3270.

[18] *Ber.*, **32**, 2862 (1900); *Z. anorg. Chem.*, **25**, 209 (1900); 29, 371 (1902); *Z. physik Chem.*, **123**, 429 (1926); Elektrochemie nichtwässriger Lösungen, 1924; solutions in H_2S, Quam, *J. Am. Chem. Soc.*, **47**, 103, 989 (1925).

[19] *Ann. Physik*, **49**, 437 (1916); *Koll. Z.*, **18**, 101 (1916); **20**, 73 (1917); **21**, 19 (1917).

[20] Partington, *J. Chem. Soc.*, **99**, 1937 (1911); Rimbach and Weitzel, *Z. physik. Chem.*, **79**, 279 (1912); Walden and Centnerzswer, *ibid.*, **39**, 513 (1902); Walden, *ibid.*, **73**, 257 (1910); Kraus and Lucasse, *J. Am. Chem. Soc.*, **44**, 1941 (1922); Archibald, *J. Chim. Phys.*, **11**, 741 (1913); Elsey, *J. Am. Chem. Soc.*, **42**, 2454 (1920); Kraus, Electrically Conducting Systems, pp. 154 ff.; numerous papers by H. C. Jones and co-workers in *Am. Chem. J.* and *J. Am. Chem. Soc.* from 1903 onwards; Müller, *Ahrens Sammlung*, **27**, 279 (1923).

At certain concentrations and above certain temperatures the conductivity decreases with rise of temperature, and at lower temperatures there is usually a maximum point.[1] At concentrations about normal, and above, the conductivity increases steadily with rise of temperature. At higher concentrations the temperature coefficients are often very high. The effects may be interpreted on the lines of increased fluidity with rise of temperature, giving rise to an increase on conductance, and decreasing ionization, giving rise to a decrease in conductance. In very dilute solutions where the ionization is great, the conductance increases with rise in temperature because of the increasing fluidity. At certain intermediate concentrations and above certain temperatures, the conductance decreases, although at much lower temperatures the curve passes through a minimum. At high concentrations the temperature coefficient is again positive. The curves in Fig. 22[2] show the results obtained with KI in methylamine at different dilutions. The approximate equality between conductance and fluidity temperature coefficients found for aqueous solutions by Kohlrausch (see p. 539) was found also for non-aqueous solutions by Walden (*loc. cit.*).

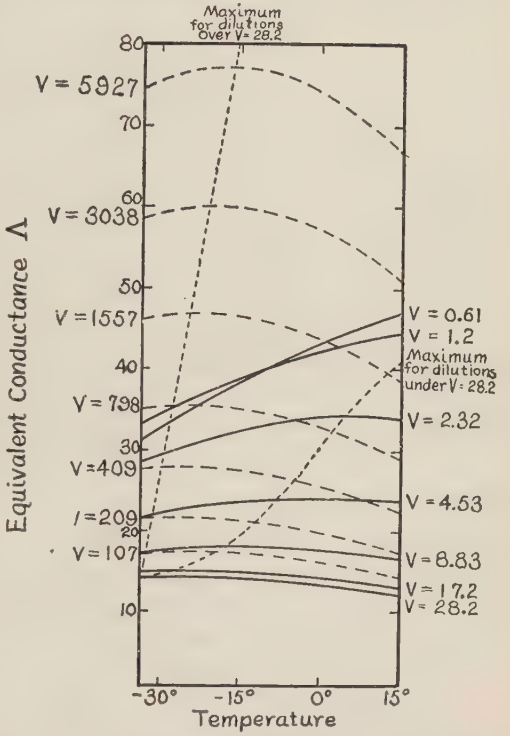

FIG. 22. Conductance-Temperature Curves for KI in Methylamine

The results of Archibald[3] in Table XV for the temperature coefficient (α) in solutions in liquid HBr at different dilutions (V) show how varied are the numerical values for different electrolytes.

The results have been interpreted by Kraus on the basis of his equation for conductance as related to concentration (see p. 657). With rise of temperature the dielectric constant of the solvent decreases, and hence the mass

[1] Kraus, *loc. cit.*, p. 154.

[2] Kraus, *loc. cit.*, Fig. 37, p. 164.

[3] *J. Chim. Phys.*, 11, 741 (1913); cf. Fitzgerald, *J. Phys. Chem.*, 16, 621 (1912); Franklin, *ibid.*, 15, 675 (1911). In the immediate vicinity of the critical point the temperature-coefficient curves are discontinuous. Apparently the solvent vapors dissolve electrolyte. Kraus, *Phys. Rev.*, 18, 40, 89 (1904); cf. Tyrer, *J. Chem. Soc.*, 97, 621 (1910) (critical points of solutions, and solubilities above the critical point).

action constant K also decreases. The value of m in the equation:

$$K' = H(c\alpha)^m + K$$

increases and H remains practically independent of the dielectric constant when the latter decreases.[1] The interpretation of the results, however, is obviously not confined to any special equation such as Kraus's.

TABLE XV

SOLUTIONS IN HBr. VALUES OF $\alpha \times 100$

	V_1	α_1	V_2	α_2
Acetic acid	4.30	2.62	0.571	2.72
Butyric acid	4.18	2.68	0.817	3.70
Benzoic acid	8.82	0.53	2.38	0.72
m-Cresol	15.0	− 7.71	1.00	+ 1.16
Thymol	43.6	0.47	7.34	0.00

The *effect of pressure* on the conductivity of non-aqueous solutions has been considered by Schmidt,[2] who divides it into three factors:

(i) change of volume; (ii) change of viscosity; (iii) change of ionization. The resistance at p atm. pressure is related to that at 1 atm. by the equation:

$$\log (r_p/r_1) = Ap - Bp^2,$$

where A, B are constants. At 20° C.,

$$A = 0.000106 + 0.00561\eta,$$

where η = viscosity for normal and slightly associated substances. In the case of strongly associated solvents (alcohols) the observed value of A is smaller; A also decreases with rise of temperature. The pressure coefficient is usually larger for aqueous solutions.

Viscosity and Conductivity: The same considerations apply to non-aqueous as to aqueous solutions with respect to the effect of viscosity on the motion of the ions. From the measurements of conductivities of solutions of tetraethylammonium iodide in various organic solvents Walden[3] was led to the generalization that the product of the molar conductance at infinite dilution and the viscosity of the solvent is constant: $\mu_\infty\eta_\infty$ = const. The constant is about 0.7, and is independent of temperature. At first Walden considered that the constant was independent of the solvent, but this was disproved by Pissarjewski and Shapovalenko.[4] Walden extends his rule to the mobilities of the separate ions: $l_\infty\eta_\infty$ = const., but although this relation holds approximately except in the case of some ions in aqueous solution, it is far from exact as the following table shows, the results being at 25° C. (Cl^- at 18°):

[1] Electrically Conducting Systems, p. 155.

[2] *Z. physik. Chem.*, **75**, 305 (1910).

[3] *Z. physik. Chem.*, **55**, 207, 246 (1906); the relation follows from Stokes's law, Lungo, *Nuovo Cim.*, **16**, ii, 173 (1918); Ulich, *Trans. Farad. Soc.*, **23**, 388 (1927).

[4] *J. Russ. Phys. Chem. Soc.*, **42**, 905 (1910); *C. A.*, **6**, 318 (1912); Walden, *Z. anorg. Chem.*, **113**, 85 (1920).

		K^+	Li^+	H^+	Cl^-	I^-	NO_3^-
Water	l	74.8	38.9	351.5	76.3	76.7	71
	$l\eta$	0.668	0.347	3.14	0.682	0.686	0.634
CH_3OH	l	53.5	39	143	52	61	61
	$l\eta$	0.292	0.213	0.779	0.284	0.332	0.332
C_2H_5OH	l	24.6	17.6	61.6	21.4	26.3	26
	$l\eta$	0.267	0.192	0.669	0.232	0.285	0.282

The empirical rule of Walden is not of general validity,[1] although it is a useful approximation which holds good in many cases. Walden[2] tested it for a large number of solutions. In the cases of $N(C_2H_5)_4I$ in benzyl cyanide, and $N(C_5H_{11})_4I$ in methyl and ethyl alcohols and acetone, the results showed that the salts of complex kations behaved exactly like KI. It was found that if V is the molar volume of a large ion, the relation $\Lambda_\infty \eta_\infty \sqrt[3]{V} = \text{const.}$ holds for different salts of a homologous series. Fitzgerald[3] applied Walden's relation to solutions in SO_2, NH_3 and methylamine. The constant fell between 0.9 and 1.1, and the conclusion was reached that these solvents are abnormal, but Walden[4] has shown that for binary electrolytes the constant may vary from 0.5 to 1.0.

Arndt[5] found that Walden's rule, $\Lambda\eta = \text{const.}$, does not hold even approximately for fused $NaPO_3$ and mixtures of this with B_2O_3, below 900°. Above this temperature the relation applies.

Walden has also shown, from a consideration of a large amount of experimental data,[6] that his rule holds for many acids and some salts in non-aqueous solvents, mixtures of solvents, and for aqueous solutions of salts yielding highly complex ions. The temperature coefficients of viscosity and of limiting conductance are practically identical:

$$1/\Lambda_\infty . d\Lambda_\infty/dt = -1/\eta_\infty . d\eta_\infty/dt,$$

as required by the rule. It does not hold for solvents which are highly associated, or which have a high viscosity, such as glycerol, formamide, etc.,[7] probably because temperature and concentration changes affect the degree of solvation of the solute. Robertson and Acree[8] find the relation

$$\alpha = \mu_v \eta_v / \mu_\infty \eta_\infty$$

to be less accurate for alcoholic solutions of concentration below $N/4$ than the

[1] Dutoit and Duperthuis, *J. Chim. Phys.*, **6**, 726 (1908); criticized by Walden, *Z. physik. Chem.*, **78**, 257 (1912).

[2] *Bull. Acad. Sci. Petersb.*, **7**, 559 (1913).

[3] *J. Phys. Chem.*, **16**, 621 (1912).

[4] *Z. anorg. Chem.*, **113**, 85 (1920).

[5] *Z. Elektrochem.*, **13**, 809 (1907).

[6] *Z. anorg. Chem.*, **113**, 85 (1920).

[7] Pissarjewsky and Shapovalenko, *J. Russ. Phys. Chem. Soc.*, **42**, 905 (1910); *C. A.*, **6**, 318 (1912).

[8] *J. Phys. Chem.*, **19**, 381 (1915).

simple Arrhenius formula: $\alpha = \mu_v/\mu_\infty$. This type of viscosity correction, in fact, is by no means so certain as seems to be assumed.[1]

H. C. Jones [2] proposed the relation $\Lambda\eta/x = \text{const.}$, where Λ is the equivalent conductance of comparable equivalent solutions and x the association factor of the solvent. This was shown by Creighton [3] to hold approximately for solutions of *p*-tolyltrimethylammonium iodide in organic solvents. The expression $\Lambda_\infty\eta = \text{const.}$, also due to Jones, held for many of the solutions.

Sachanov and Prsheborovski,[4] as a result of experiments with solutions of silver nitrate in amylamine, aniline, quinoline, and other solvents, conclude that the maximum conductance shown by these solutions is a consequence of the overcompensation of the increase in dissociation of the solute by the excessive increase in viscosity of the solutions with concentration. The abnormality disappears when a viscosity correction is applied. In solvents with low dielectric constants (less than 13) the viscosity increases very rapidly with concentration. With solvents of high dielectric constant the molar conductance diminishes uninterruptedly with concentration, whilst if a viscosity correction is applied a minimum conductance is found.

Dielectric Constant and Conductance: The force exerted between two charged point sources depends not only on the charges, q_1, q_2, and the distance d apart, but also, as was shown by Faraday,[5] on the nature of the medium separating them:

$$F = q_1q_2/Dd^2,$$

where D is a constant for any particular medium, known as the dielectric constant (called the specific inductive capacity by Faraday). Its value depends on temperature. The following values [6] refer to 18° C.

TABLE XVI

Dielectric Constants of Liquids

Liquid Hydrocyanic acid	96	Methylamine	10
Water	81	Phenol	9.7
Nitrobenzene	36	Acetic acid	9.7
Methyl alcohol	33	Aniline	7.28–7.5
Ethyl alcohol	26	Propionic acid	5.5
Ammonia	22	Chloroform	5
Sulphur dioxide	16.5	Ether	4
Pyridine	12.4	Carbon disulphide	2.6
Ethylene chloride	10	Benzene	2.3

[1] King and Partington, *Trans. Farad. Soc.*, **23**, 531 (1927); Hatschek, The Viscosities of Liquids, 1928, p. 180.

[2] *Am. Chem. J.*, **32**, 521 (1904); Jones and Bingham, *ibid.*, **34**, 481 (1905), pointed out that no allowance was made for possible changes in size of the ionic sphere.

[3] *J. Franklin Inst.*, **187**, 313 (1919).

[4] *J. Russ. Phys. Chem. Soc.*, **47**, 849 (1915); *C. A.*, **9**, 3009 (1915).

[5] Experimental Researches in Electricity, 11th Series, pp. 364, 393.

[6] Numerous other liquids, Schlundt, *J. Phys. Chem.*, **5**, 157, 503 (1901); Winkelmann's Physik, Vol. IV, 1905, pp. 135 ff.; also Graetz, Elektrizität und Magnetismus, Vol. I, 1918, pp. 157 ff.; Müller, *Ahrens Sammlung*, **27**, 243, 285 (1923); Grimm and Patrick, *J. Am. Chem. Soc.*, **45**, 2794 (1923); *International Critical Tables*; Landolt-Börnstein, *Tabellen*.

A comparison of these numbers with the ionizing powers of the solvents reveals a close similarity, which seems first to have been pointed out by J. J. Thomson [1] and Nernst,[2] and is known as the Nernst-Thomson rule: the ionizing power of a solvent is greater the larger the dielectric constant. The equation shows that the force between the pair of ions forming the salt "molecule" is smaller the larger the dielectric constant of the medium in which they are immersed, and they then fall apart more easily. The Nernst-Thomson rule has been broadly confirmed by experiment.[3] There are other influences promoting ionization, and these appear most markedly when the dielectric constant is small; the chemical character of the solvent is then most important.[4] The dielectric constants of halogen hydrides (HBr, HI) are abnormally low, yet these solvents give solutions of high conductance with certain organic acids and alcohols.[5]

The methods used in the determination of dielectric constants are:

(1) The condenser method, in which the capacity of a condenser is measured first with air as the dielectric and then with the liquid.[6] The dielectric constant of air may be taken as unity.

(2) The stationary wave method, in which [7] the lengths of stationary electromagnetic waves set up in the medium and in air are measured, the length being inversely proportional to $\sqrt{D}$.

The dielectric constants of many solvents have been measured by Walden,[8] who has also calculated the value for dissolved salts.[9] Formulæ have been

[1] *Phil. Mag.*, **36**, 320 (1893).

[2] *Z. physik. Chem.*, **13**, 531 (1894).

[3] Schlundt and Palmer, *J. Phys. Chem.*, **15**, 381 (1911); Sachanov and Prsheborovski, *Z. Elektrochem.*, **20**, 39 (1914); Joachim, *Ann. Physik*, **60**, 570 (1919).

[4] Sachanoff, *J. Russ. Phys. Chem. Soc.*, **42**, 1363 (1910); *C. A.*, **6**, 179 (1912); **43**, 526 (1911); *C. A.*, **6**, 179 (1912); *Z. physik. Chem.*, **80**, 13, 20 (1912); cf. Plotnikoff and Rokotjan, *ibid.*, **45**, 193 (1913); *C. A.*, **7**, 2148 (1913); *ibid.*, **47**, 723 (1915); *C. A.*, **8**, 2475 (1914).

[5] Schaefer and Schlundt, *J. Phys. Chem.*, **13**, 669 (1909).

[6] Nernst, *Z. physik. Chem.*, **14**, 622 (1894); Turner, *ibid.*, **35**, 385 (1900); Tangl, *Ann. Physik*, **23**, 559 (1907); Joachim, *ibid.*, **60**, 570 (1919); for descriptions of all methods see Nernst, Theoretische Chemie, 8–10 Aufl., p. 367; Kohlrausch, Praktische Physik, 11 Aufl., pp. 616 ff.; Arndt, Physikal-Chem. Technik, 1915, pp. 611 ff.; Graetz, *loc. cit.;* Winkelmann, *loc. cit.* Other methods: Hertwig, *Ann. Physik*, **42**, 1099 (1913); Jackson, *Phil. Mag.*, **43**, 481 (1922); King and Patrick, *J. Am. Chem. Soc.*, **43**, 1835 (1921); Silow's electrometer method, Cohn and Arons, *Ann. Physik*, **33**, 13 (1888); Williams and Krchma, *J. Am. Chem. Soc.*, **48**, 1889 (1924)—valve-oscillator circuit; *ibid.*, **49**, 2408 (1927); Williams and Ogg, *ibid.*, **50**, 94 (1928); Smyth, Morgan and Boyce, *ibid.*, 1536; Sayce and Briscoe, *J. Chem. Soc.*, **127**, 315 (1925); Fürth, *Z. Physik*, **44**, 256 (1927); Kniekamp, *Z. Physik*, **51**, 95 (1928); Hedestrand, *Z. physik. Chem.*, **135**, 36 (1928); Carman, *Phys. Rev.*, **24**, 396 (1924); Harris, *J. Chem. Soc.*, **127**, 1049 (1925); Schulwas-Sorokina, *Z. Physik*, **48**, 426 (1928); Toshikatsu Matsuike, *Sci. Rep. Tohoku Univ.*, **14**, 445 (1925).

[7] Drude, *Z. physik. Chem.*, **23**, 267 (1897); **40**, 635 (1902); Voigt, *Z. Physik*, **44**, 71 (1927); Fürth, *Ann. Physik*, **70**, 63 (1923); Bock, *Z. Physik*, **31**, 534 (1925); Hellmann and Zahn, *Physik. Z.*, **26**, 680 (1925); **27**, 636 (1926); *Ann. Physik*, **80**, 182, 191 (1926); **81**, 711 (1926); **81**, 711 (1926); **86**, 687 (1928).

[8] *Z. physik. Chem.*, **70**, 569 (1910); Schaefer and Schlundt, *J. Phys. Chem.*, **13**, 669 (1909); **16**, 253 (1912); Schlundt and Underwood, *ibid.*, **19**, 338 (1915); Cauwood and Turner, *J. Chem. Soc.*, **107**, 276 (1915); Ratz, *Z. physik. Chem.*, **19**, 94 (1896); Schlundt, *loc. cit.*

[9] *Bull. Acad. Sci. Petersb.*, **6**, 305, 1055 (1912).

proposed for the dielectric constants of solutions, e.g., by Silberstein:[1]

$$D = (V_1D_1 + V_2D_2)/(V_1 + V_2),$$

the mixture rule, and by Bouty:[2]

$$D = (M_1D_1 + M_2D_2)/(M_1 + M_2),$$

with masses instead of volumes.

The molar conductance of many solutions in solvents of small dielectric constant decreases with dilution. Solvents of high dielectric constant often show a negative viscosity effect, i.e., the viscosity of solutions decreases with increasing concentration.[3]

Dobrosserdoff[4] has found that Obach's relation:[5] $L = aD$, where L = latent heat of evaporation and a is a constant in a given homologous series (39.5 for aliphatic acids; 25.5 for amines; 31 for aromatic hydrocarbons; 14.2 for all esters; 6.5 for alcohols, nitriles,[6] ketones and alkyl halides), is of fairly wide applicability. Thwing's relation:

$$D = d(a_1k_1 + a_2k_2 + \cdots)/M,$$

where d = density, M = molar weight, a_1, a_2, $\cdots$ = number of atoms, k_1, k_2, $\cdots$ = dielectric constants of separate atoms, does not hold generally. Lang's relation:

$$D = 121.10^{-6}S + 1,$$

where S = sum of valencies of atoms, holds only for six gases. The same author has reached the following general conclusions as to the dielectric constant:[7] (1) It is a constitutive property. (2) In homologous series it decreases with increasing molecular weight.[8] (3) Large differences in D are produced by multivalent elements, e.g., nitrogen. (4) The effect on D produced by the entry of any one radical into a compound varies with the compound. (5) Change from a saturated to an unsaturated compound is accompanied by increase in D. (6) D increases with the symmetry of the compound, e.g., ring closure increases D. (7) Isomeric compounds have different D's.

[1] *Ann. Physik*, **56**, 661 (1895); cf. Salazar, *Anal. Fis. Quim.*, **22**, 275 (1924); Lichtenecker, *Physik. Z.*, **27**, 115 (1925)—exhaustive bibliography for mixtures; Grutzmacher, *Z. Physik*, **28**, 342 (1924).

[2] *Compt. rend.*, **114**, 1421 (1892); Philip, *Z. physik. Chem.*, **24**, 18 (1897). Dobroserdoff, *J. Russ. Phys. Chem. Soc.*, **44**, 396, 679 (1912); *C. A.*, **6**, 1564, 2350 (1912), finds that the formulæ are not satisfactory; cf. Fürth, *Ann. Physik*, **70**, 63 (1923), who found, for instance, that the constant for a crystalline solute cannot be found from the mixture rule.

[3] Sachanov and Prsheborovski, *Z. Elektrochem.*, **20**, 39 (1914); Kraus and Bray, *J. Am. Chem. Soc.*, **35**, 1315 (1913).

[4] *J. Russ. Phys. Chem. Soc.*, **41**, 1385 (1909); *C. A.*, **5**, 607 (1911).

[5] Cf. Grimm and Patrick, *J. Am. Chem. Soc.*, **45**, 2794 (1923).

[6] Cf. Schlundt, *J. Phys. Chem.*, **5**, 503 (1901).

[7] *J. Russ. Phys. Chem. Soc.*, **43**, 73 (1911); cf. *C. A.*, **5**, 3362 (1911).

[8] Eversheim, *Ann. Physik*, **8**, 539 (1902); **13**, 492 (1904).

According to the theory of Clausius [1] and Mossotti, the molecules of a dielectric are assumed to be electrically conducting spheres, causing a diminution in the force between two charges in the medium. If u is the fraction of the total volume of the dielectric which is occupied by the molecules, it is found that:

$$u = (D - 1)/(D + 2).$$

Rise in temperature diminishes D in the case of liquids and gases, but increases it in the case of solids. According to Thomson [2] the change in D for liquids and gases is inversely proportional to the absolute temperature. The dielectric constants at the critical temperature are very small.[3]

Fleming and Dewar [4] measured the dielectric constants of several liquids at low temperatures; the constant for the solidified substance appears to decrease as the temperature falls.

The effect of pressure for liquids is given by the empirical formula: [5]

$$D_p = D_1(1 + Ap + Bp^2),$$

in which A is positive and B negative.

	MeOH	EtOH	Me_2CO	Et_2O	CS_2	$C_6H_5NH_2$
D at 15° C.	34.0	25.8	21.85	4.25	2.67	7.51
D at − 185° C.	3.13	3.11	2.12	2.31	2.24	2.92

The figures for ice are:

t° C.	− 206	− 182	− 175	− 149	− 136	− 111	− 77.7	− 49.0	− 7.5
D_t	2.43	2.42	2.43	3.43	5.02	10.8	37.3	57.2	70.8

Walden [6] has put forward the approximate rule:

$$(1 - \alpha) = \text{const. } c^{1/3}/D,$$

[1] Clausius, *Ges. Abh.*, ii, 135 (1867); Pagliani, *Atti dei Lincei*, **2**, 48 (1893).

[2] *Phil. Mag.*, **27**, 764 (1914); Bell and Poynton, *ibid.*, **49**, 1065 (1924) give $D\theta = D_{20} \times [1 - (\theta - 20)\alpha]$; Kockel, *Ann. Physik*, **77**, 417 (1925); Debye, *Verh. phys. Ges.*, **15**, 777 (1913).

[3] Eversheim, *Ann. Physik*, **8**, 539 (1902); **13**, 492 (1904).

[4] *Proc. Roy. Soc.*, **61**, 299, 316, 358, 368 (1897);:Onnes and others, *Proc. K. Akad. Wet. Amst.*, **27**, 617, 621, 627 (1924)—liquid He, H_2, O_2, liquid and solid H_2 : for H_2, D increases with falling temperature to near the m.pt., when it teaches a maximum and then decreases for solid H_2 with fall in temperature. The results agree with the Clausius-Mossotti formula; Frenacher, *Ann. Physik*, **77**, 138 (1925); Francke, *ibid.*, 159.

[5] Ortway, *Ann. Physik*, **36**, 1 (1911); ether, benzene, toluene, xylene, CS_2, castor oil, etc.; Cf. Kyropoulos, *Z. Physik*, **40**, 507 (1927)—up to 3000 Kg./cm². to test the formula $(D - 1)/(D + 2) \times 1/d = f(p)$, where d = density; Cagniard, *Compt. rend.*, **183**, 873 (1926)

[6] Walden, *Z. physik. Chem.*, **94**, 263, 295, 374 (1920); **54**, 129 (1906); **70**, 569 (1910).

where c is the concentration, or $Dv^{1/3}$ = const. at a given temperature, for different solvents, where v is the dilution at which the solutions of a given electrolyte have the same ionization. The values of the "constant" vary by as much as 23 per cent,[1] and Walden's rule cannot hold generally.

If K is the constant of the Ostwald dilution law at infinite dilution $K = (0.0054D)^3$, or generally, K = const. D^3. It follows that similar formulæ hold for polymerizing solvents.[2]

The influence of small quantities of salts on the dielectric constants of solvents has been studied by many experimenters.[3] Recent experiments of Walden and co-workers, and of Pechold, indicate that the presence of small amounts of electrolyte causes a fall in the dielectric constant of the solvent, due probably to the fixing of orientated dipoles about the ions. With increasing concentration, the value of D may reach a minimum after which it rises again and may exceed the value for the pure solvent. This is interpreted as due to the presence of complex ions, "conglomerations of ions of both signs." Pechold finds that with large concentrations of salt, D reaches a saturation value. Walden, whose results have been criticized by Hellmann and Zahn, represents his results on the falling part of the curve by an equation of Hückel:

$$D_0 - D = 2\delta c,$$

and proposes

$$\delta/D_s = D_0^{3/2},$$

where D_s is the value for the saturated solution. Different observers find very different values of δ, e.g., from 3 (calculated by Hückel) to 6000 (Fürth), and Hückel's equation is now generally agreed to be unsatisfactory, except perhaps in *very* dilute solutions.

Maxwell [4] deduced the relation $n = D^{1/2}$, where n = refractive index, from the electromagnetic theory of light. This is in agreement with experiment in some cases, but the divergencies are enormous in the case of water and alcohol. The divergencies are attributed to the difference in the frequencies in the light waves and those used in finding the values of D. For very long waves, n has the required value for water.

[1] Partington, *Trans. Farad. Soc.*, **15**, 113 (1919); Kraus, Electrically Conducting Systems, p. 97; Turner and Bissett, *J. Chem. Soc.*, **105**, 947 (1914).

[2] Walden, *Z. physik. Chem.*, **94**, 263, 295, 374 (1920); **54**, 129 (1906); **70**, 569 (1910).

[3] Cohn, *Ann. Physik*, **45**, 370 (1892); Nernst, *Z. physik. Chem.*, **14**, 622 (1894); Drude, *ibid.*, **23**, 267 (1897); Smale, *Ann. Physik*, **61**, 625 (1897); Palmer, *Phys. Rev.*, **14**, 38 (1902); Walden, *Bull. Acad. Sci. Petersb.*, **6**, 305, 1055 (1912); Lattey, *Phil. Mag.*, **41**, 829 (1921); Sack, *Physik. Z.*, **28**, 199 (1927); Skancke and Schreiner, *ibid.*, **28**, 597 (1927); Pechold, *Ann. Physik*, **83**, 427 (1927); Walden, Ulich and Werner, *Z. physik. Chem.*, **116**, 261 (1925); **115**, 177 (1925); Walden and Ulich, *ibid.*, **110**, 43 (1924); Ulich, *Z. Elektrochem.*, **31**, 413 (1925); Hellmann and Zahn, *Z. physik. Chem.*, **132**, 399 (1928); *Ann. Physik*, **86**, 687 (1928); LaMer, *Trans. Electrochem. Soc.*, 1928; Hückel, *Physik. Z.*, **26**, 93 (1925); Fürth, *ibid.*, **25**, 676 (1924); Zahn, *Z. Physik*, **31**, 362 (1925); Walden and Werner, *Z. physik. Chem.*, **124**, 465 (1926); **129**, 389, 405 (1927); Walden, Ulich and Werner, *ibid.*, 417; Redlich, *Physik. Z.*, **26**, 199 (1925); Gross and Halpern, *ibid.*, 403, 636.

[4] Electricity and Magnetism, Oxford, 1892, Vol. II, pp. 434 ff.

Clausius and Mosotti's [1] relation leads to:

$$(D - 1)/(D + 2)d = \text{const.},$$

where d is the density. Walden [2] finds that the constant varies with temperature, sometimes increasing and sometimes decreasing with rise of temperature. He proposes the empirical relations:

$$\frac{D - 1}{D + 2} \cdot \frac{M}{d} \frac{\sigma}{T_s} = \text{const.} = 3.6,$$

where T_s is the absolute boiling point, and σ is the surface tension, and

$$MD = 0.18T_s.$$

These do not hold for associated liquids.

Solvents with considerable ionizing power have a strong tendency to associate in the liquid state; [3] this agrees with the observation of Kohlrausch that pure liquids do not conduct at ordinary temperature to any appreciable extent. The degree of association of a binary solute in a non-aqueous solvent depends on the dielectric constant, increasing with falling dielectric constant.[4] Walden concludes that highly associated binary electrolytes may pass through all stages of molecular complexity, from simple ions to highly complex molecules, in suitable solvents. Sodium chloride in benzene is colloidal.

The Nature of Non-Aqueous Solutions: After the successful application of Arrhenius' theory of electrolytic dissociation to aqueous solutions it seemed obvious that the results obtained with other solvents should be capable of interpretation in a similar way. With the progress of investigation, however, serious difficulties were encountered. In some cases the molar conductance diminishes with increasing dilution, instead of increasing to a limit as it should on the theory of ionization. In the early days of the ionic theory the assumption was made that all reactions are ionic, and the curious arrest of many reactions in carefully dried systems lent some support to this sweeping generalization. Careful experiments showed [5] that reactions can take place in non-aqueous solutions which show no trace of conductance. On the other hand, earlier experiments of this type,[6] brought up as evidence against the ionic theory, have been shown [7] to be incorrect; solutions of copper salts in dry benzene have a definite conductance.

[1] Mechanische Wärmetheorie (Clausius), 1876, Vol. 2, p. 94. Cf. Pagliani, *Acc. dei Lincei*, **2**, 48 (1893).

[2] *Z. physik. Chem.*, **70**, 569 (1910).

[3] Nernst, *Z. physik. Chem.*, **14**, 622 (1894); Dutoit and Aston, *Compt. rend.*, **125**, 240 (1897); Kohlrausch, *Ann. Physik*, **159**, 270 (1875).

[4] Meldrum and Turner, *J. Chem. Soc.*, **93**, 876 (1908); **97**, 1605, 1805 (1910); Walden, *Kolloid Z.*, **27**, 97 (1920).

[5] Folin and Flanders, *J. Am. Chem. Soc.*, **34**, 774 (1912).

[6] Kahlenberg, *J. Phys. Chem.*, **5**, 339 (1901); **6**, 1 (1902); cf. Hughes, *Phil. Mag.*, **35**, 533 (1893); Sammis, *J. Phys. Chem.*, **10**, 593 (1906); Gates, *ibid.*, **15**, 97 (1911).

[7] Cady and Lichtenwalter, *J. Am. Chem. Soc.*, **35**, 1434 (1913).

Other experimenters [1] report that a limiting molar conductance is not reached at high dilution with electrolytes in non-aqueous solutions, whereas Robertson and Acree,[2] and Dhar and Bhattacharyya [3] obtained definite limiting conductances.

The question of the calculation of ionization from conductance has also received different answers. Kraus and Bray [4] consider that the ratio of molar to limiting conductance measures the ionization up to 1 n. when corrections for viscosity are applied. On the other hand, Snethlage[5] considers that solutions in ethyl and methyl alcohols may be divided into two groups: (1) strong electrolytes, such as HCl and salts, the properties of solutions of which are functions of the total concentration of electrolyte; (2) most organic bases and acids, which do not show this proportionality. For the first class, the ionization, it is stated, cannot be measured by the ratio of the conductances, but this ratio expresses the ratio of active to inactive molecules. The "activation" of a molecule is explained by the introduction of an electron into it, rendering it bipolar, but no division into free ions takes place. Snethlage's view does not seem to afford much assistance in the study of solutions. It may also be noted that the interpretation of ionization phenomena from results in chemical kinetics (velocity of reaction) is a matter of great delicacy, and that conclusions drawn in this field must be accepted with some caution.

Walden [6] found that the value of $\alpha = \Lambda/\Lambda_\infty$ (Λ_∞ obtained by extrapolation) is the same (0.666) for *saturated* solutions of NMe_4I, NEt_4I, and NPr_4I in different solvents.

The question of the applicability of the law of mass action to non-aqueous solutions has been fairly exhaustively studied.[7] In some cases the Ostwald dilution law is followed. Thus, solutions of ammonium formate in anhydrous formic acid obey the law in concentrated solutions; [8] fairly concentrated solutions of rosaniline hydrochloride in ethyl and methyl alcohols follow the law,[9] although aqueous solutions do not. In other cases the Rudolphi dilution law (p. 657) can be applied.[10] The equation of Kraus and Bray (see p. 657) has been applied to non-aqueous solutions with some success. In many solutions in

[1] Shaw, *J. Phys. Chem.*, **17**, 162 (1913); cf. Plotnikoff, *J. Russ. Phys. Chem. Soc.*, **42**, 1589 (1910).

[2] *Eighth Internat. Congress Appl. Chem.*, **26**, 609 (1912).

[3] *Z. anorg. Chem.*, **82**, 357 (1913).

[4] *J. Am. Chem. Soc.*, **35**, 1315 (1913); see the admirable discussion of the problem in Kraus, Electrically Conducting Systems, 1922.

[5] *Z. physik. Chem.*, **90**, 1 (1915); Snethlage's hypothesis has been subjected to severe criticism by Dhar, *Trans. Farad. Soc.*, **15**, 81 (1919).

[6] *Bull. Acad. Sci. Petersb.*, **7**, 427 (1913).

[7] See the summary by Kraus, Electrically Conducting Systems, also Walden, Nichtwässriger Lösungen, 1924.

[8] Schlesinger and Calvert, *J. Am. Chem. Soc.*, **33**, 1924 (1911).

[9] H. S. Davis, *Trans. Nova Scotia Inst. Sci.*, **13**, 40 (1912); cf. Robertson and Acree, *J. Phys. Chem.*, **19**, 381 (1915); Neale, *Trans. Farad. Soc.*, **17**, 505 (1922); Jones and Mahin, *Z. physik. Chem.*, **69**, 389 (1909); Schlesinger and Reed, *J. Am. Chem. Soc.*, **41**, 1921 (1919); Schlesinger and Martin, *ibid.*, **36**, 1589 (1914).

[10] Roshdestwensky and Lewis, *J. Chem. Soc.*, **99**, 2138 (1911).

ammonia the law of mass action holds good, and the smaller the ionization of an electrolyte the higher is the total concentration up to which the law of mass action applies.[1] This, it may be noted, is in agreement with the theory proposed by the writer[2] that the deviations from the law of mass action are due to free ions, and Kraus and Bray found that the limiting concentration of the ions of strong electrolytes up to which the mass law held was approximately the same for solutions of a given electrolyte in different solvents, and for different electrolytes (strong and weak) in the same solvent.

The effect of the dielectric constant on the constants of the Kraus and Bray equation appears to be fairly regular. The equation has been tested in a number of cases,[3] and found to be generally satisfactory. The existence of a true dissociation constant, K, at high dilution for all electrolytes has been inferred. On the other hand, the empirical Storch equation (p. 658), which does not lead to a true dissociation constant at first dilutions, gives equally satisfactory results.[4] For very dilute solutions Walden and Ulich[5] found the two equations of Kohlrausch (p. 654):

$$\Lambda = \Lambda_0 - ac^{1/3} \qquad \text{and} \qquad \Lambda = \Lambda_0 - bc^{1/2}$$

to apply to non-aqueous solutions. The second equation agrees with the Debye-Hückel theory (p. 661). At moderate concentrations the very exact work of Völlmer[6] showed that an equation of the type

$$\Lambda_0 = \Lambda + ac^{1/3} + bc^{2/3}$$

was required.[7]

Walden[8] considers that the heat of ionization of a salt has the same value in different solvents, but this has been contradicted by Dutoit and Aston.[9] Different heats of ionization would imply interaction with solvent.

Calculations of the diameters of ions in non-aqueous solvents have been made by Walden[10] on the basis of the Stokes-Einstein equation (p. 688). For most ions the radii lie between 2.0×10^{-8} cm. and 3.9×10^{-8} cm., although that of the $H^{\cdot}$ ion is much smaller, 1.1×10^{-8} cm., and that of the $Li^{\cdot}$ ion much larger, 4.70×10^{-8} cm. The ionic radii in non-aqueous solutions follow the same order as in aqueous solutions: $H^{\cdot} < K^{\cdot} < Ag^{\cdot} < Na^{\cdot} < Li^{\cdot}$ and $Br' < I' < Cl' < NO_3'$. The ionic and atomic radii are practically the same, except for $H^{\cdot}$ and $Li^{\cdot}$, in the case of aqueous solutions, but in non-aqueous

[1] Kraus and Bray, *J. Am. Chem. Soc.*, **35**, 1315 (1913).

[2] Partington, *J. Chem. Soc.*, **97**, 1158 (1910).

[3] Keyes and Winninghoff, *J. Am. Chem. Soc.*, **38**, 1178 (1916); Darby, *ibid.*, **40**, 347 (1918); Kraus and Kurtz, *ibid.*, **44**, 2463 (1922); Kraus, Electrically Conducting Systems, 1922, pp. 67 ff.

[4] Ferguson and Vogel, *Trans. Farad. Soc.*, **23**, 414 (1927).

[5] *Z. physik. Chem.*, **114**, 297 (1924).

[6] *Ann. Physik*, **52**, 328 (1894).

[7] Cf. Hawkins and Partington, *Trans. Farad. Soc.*, **24**, 518 (1928).

[8] *Z. physik. Chem.*, **59**, 192 (1907).

[9] *J. Chim. Phys.*, **6**, 699 (1908); Walden, *Z. physik. Chem.*, **78**, 257 (1912), maintains his position.

[10] *Z. anorg. Chem.*, **113**, 125 (1920).

solutions the ionic radii are about twice as great. With organic anions and kations the radii are about the same in water and other solvents, the mean value being about 4.4×10^{-8} cm.

Walden [1] has put forward a rule by means of which the ionization of a salt in any solvent may be calculated from the dielectric constant D and viscosity η of the latter. This is a combination of the Ostwald-Bredig rule, and the relation

$$\Lambda_\infty = \Lambda_v + b/v^{0.45}$$

put forward by Lorenz.[2] These were combined with the relation

$$K = d_v D \eta_\infty v^{0.45}$$

found by Walden, in which d_v is given by the Ostwald-Bredig rule: $\Lambda_\infty = \Lambda_v + d_v$. Thence:

$$(1 - \alpha) D . v^{0.45} = 51.4/\Lambda_\infty \eta_\infty$$

or, since $\Lambda_\infty \eta_\infty$ is constant for many solutions (p. 591), it follows that:

$$(1 - \alpha) D . v^{0.45} = \text{const.},$$

or, for the same solvent,

$$(1 - \alpha) v^{0.45} = \text{const.}$$

Thus, if the value of $\Lambda_\infty \eta_\infty$ is known for a salt in any one solvent, the value of α in any other solvent at a given dilution may be calculated.[3]

Solvation: [4] The solvation hypothesis of Kohlrausch (p. 689) [5] has been extended to non-aqueous solutions.[6] Snethlage [7] considers that a large value of Λ_∞ indicates large solvation. Jones, Davis and Putnam [8] found that salts hydrated in aqueous solutions show evidence of solvation in formamide. The temperature coefficient of conductance is abnormally large when solvation is present. The temperature coefficient of conductance of sodium salts in ethyl alcohol is equal to the temperature coefficient of fluidity [9] between 0° and 30°, in agreement with Kohlrausch's theory.

Serkoff [10] pointed out that a compound such as lithium nitrate, the Li ion of which shows strong solvation, should exhibit a maximum conductance in mixtures of acetone and an alcohol, whilst potassium iodide should show no maximum. The salts KI, NaI and LiI showed no maximum, whilst LiCl did.

[1] *Z. anorg. Chem.*, **115**, 49 (1921).

[2] *Z. anorg. Chem.*, **108**, 81, 191 (1919).

[3] Relation between solvent power and ionizing power: Walden, *Z. Elektrochem.*, **27**, 34 (1921). Sachanov, *J. Russ. Phys. Chem. Soc.*, **47**, 849, 859 (1915), considers that the ionization of a salt tends to a definite limit as the concentration increases.

[4] Cf. Müller, *Ahrens Sammlung*, **27**, 292 (1923).

[5] *Proc. Roy. Soc.*, **71**, 338 (1903)

[6] Jones and Carroll, *Am. Chem. J.*, **32**, 521 (1904); Jones, *ibid.*, **41**, 19 (1909).

[7] *Z. physik. Chem.*, **90**, 1 (1915).

[8] *J. Franklin Inst.*, **180**, 567 (1915).

[9] Bhattacharyya and Dhar, *Proc. K. Akad. Wetensch. Amst.*, **18**, 373 (1915).

[10] *J. Russ. Phys. Chem. Soc.*, **42**, 1 (1910); *Chem. Soc. Abs.*, 1910, **98**, (ii), 177.

An attempt to calculate solvation has been made by Walden,[1] who found that

$$\Lambda_\infty \eta_\infty / \sqrt{M} = \text{const.} = 11.15 \text{ (approx.)}$$

held for many binary salts, mainly iodides, in a number of non-aqueous solvents (M = molar weight). If these salts are regarded as normal, the degree of solvation of other salts can be calculated in a manner similar to that used by Ramsay for associated liquids, and with similar uncertainty. An equation deduced by Herzog[2] may be used for the same purpose:

$$\Lambda_\infty \eta_\infty v^{1/3} = \text{const.},$$

where v = molar volume of salt. It gives practically the same results as Walden's.

Transport Numbers in Non-Aqueous Solutions: The method of determining transport numbers is essentially the same for non-aqueous as for aqueous solutions. The resistance is usually greater, so that there is greater danger of heating and convection, and it has also been found[3] that the middle portion of the solution, which should remain unchanged in composition, is usually situated near one of the electrodes, e.g., in the case of pyridine and acetonitrile solutions of silver nitrate, near the anode.[4]

Sachanov and Grinbaum used aniline (D = 6.85) and mixtures of aniline and pyridine (D = 8.0 and 9.7) with silver nitrate. The transport number of silver diminished with increasing concentration for $AgNO_3$ in pyridine, acetonitrile, and the mixtures of aniline and pyridine, and for a given concentration was smaller the smaller was D. In aniline, the transport number increased with dilution, which may be connected with the formation of complex anions, of the type $Ag(NO_3)_2'$, and also complex kations. Krumreich[5] determined the transport numbers of $AgNO_3$ (0.01 n.) in mixtures of alcohol and water, by the direct method. The value of the transport number of the kation increased with the alcohol content up to about 30 per cent alcohol, and then decreased (at 40° C. with water, 0.4820; with 99.8 per cent alcohol, 0.4100). No secondary effects were noted, whereas Carrara[6] states that these occur.

[1] *Z. Elektrochem.*, **26**, 65 (1920); cf. Creighton, *J. Franklin Inst.*, **189**, 641 (1920).

[2] *Z. Elektrochem.*, **16**, 1003 (1910).

[3] Cf. Schlundt, Getman and Gibbons (refs. below).

[4] Methods of determination, see, e.g., Hittorf, *Ann. Physik*, **106**, 551 (1859); Campetti, *Nuovo Cim.*, **35**, 225 (1894); Mather, *Am. Chem. J.*, **26**, 473 (1901); Schlundt, *J. Phys. Chem.*, **6**, 159 (1902); Getman and Gibbons, *J. Am. Chem. Soc.*, **36**, 1640 (1914); Sachanov and Grinbaum, *J. Russ. Phys. Chem. Soc.*, **47**, 1769 (1915); *C. A.*, **10**, 2822 (1916); Krumreich, *Z. Elektrochem.*, **22**, 446 (1916); Frycz and Tolloczko, *Festschrift Univ. Lemberg*, **1**, 1 (1912); *Chem. Soc. Abstr.*, ii, 380 (1913); Sachanov, *J. Phys. Chem.*, **21**, 169 (1917); Schlesinger and Bunting, *J. Am. Chem. Soc.*, **41**, 1934 (1919); Franklin and Cady, *ibid.*, **26**, 499 (1904); Campetti, *Jahrb. Elektrochem.*, **1**, 22 (1895); Hartley and Raikes, *Trans. Farad. Soc.*, **23**, 393 (1927); Ulich, *ibid.*, 388; *Fortschritte der Chemie, Physik. u. physik. chem.*, **18**, Nr. 10 (1926); Drucker and Schingnitz, *Z. physik. Chem.*, **122**, 149 (1926); determinations by E. M. F. methods, see Vol. 2.

[5] *Z. Elektrochem.*, **22**, 446 (1916).

[6] *Gazz.*, **33**, 241 (1903); for criticism of Carrara's results see Lapworth and Partington, *J. Chem. Soc.*, **99**, 1417 (1911).

Kohlrausch's law of the independent mobilities of ions (p. 672) has been found to hold for a number of non-aqueous solutions.[1]

Krüger [2] concluded, on theoretical grounds, that the transport numbers of a given pair of ions should tend to the same value in all non-associated solvents. In associated solvents, and when solvation occurs, the values differ. He remarks that in dilute solutions the transport numbers of silver nitrate are practically independent of the nature of the solvent.[3] Krüger believes that the effect of the solvent may be covered, in the simple case, by its viscosity: $u\eta = c_1$ and $v\eta = c_2$, where u and v are the mobilities and c_1, c_2 are constants.

The assumption that ions with large transport numbers are those common to solute and solvent [4] is probably true only in exceptional cases.[5] According to Newbery the transport numbers of most ions, but not $H^{\cdot}$, have the same value in alcohol as in water, but this is definitely contradicted by other experiments, as shown in the table below: [6]

Solvent	Transport number of anion of		
	KCl	KI	$AgNO_3$
H_2O	0.502	0.505	0.579
CH_3OH	0.493	0.532	0.540
C_2H_5OH	0.460	0.514	0.605
Acetone	0.600	0.625	——
Pyridine	——	0.610	——

Conductance in Mixed Solvents: Many measurements of conductance have been made [7] in mixed solvents, but the results are not easy to interpret. Several measurements with mixtures of water and alcohol are available.[8] The con-

[1] Carrara, *Atti R. accad. Lincei*, **4**, 339 (1901)—methyl alcohol; Walden, *Z. physik. Chem.*, **54**, 129 (1906)—acetonitrile and epichlorhydrin; Dutoit and Gyr, *J. Chim. Phys.*, **7**, 189 (1909)—sulphur dioxide; Hartley and Frazer, *Proc. Roy. Soc.*, **109A**, 351 (1925)-methyl alcohol; Ulich, *Trans. Farad. Soc.*, **23**, 388 (1927)—summary; Hartley and Raikes, *ibid.*, 393-methyl alcohol; Nonhebel and Hartley, *Phil. Mag.*, **2**, 729 (1925)-methyl alcohol; Walden, Leitvermögen der Lösungen, Part I, 1924, p. 321.

[2] *Z. Elektrochem.*, **22**, 445 (1916); Tibor Erdey-Grúz, *Z. physik. Chem.*, **131**, 81 (1928).

[3] Sachanov, *J. Phys. Chem.*, **21**, 169 (1917).

[4] Danneel, *Z. Elektrochem.*, **11**, 125, 249 (1905); Lorenz, *Z. physik. Chem.*, **73**, 255 (1910); **82**, 615 (1913); Frycz and Tolloczko, *Festscrift Univ. Lemberg*, **1**, 1 (1912); *Chem. Soc. Abstr.*, ii, 380 (1913).

[5] Walden, *Z. Elektrochem.*, **26**, 72 (1920); Tijmstra, *Z. physik. Chem.*, **49**, 347 (1904); Shikata, *Trans. Farad. Soc.*, **19**, 721 (1923). The assumed "Grotthuss effect" thus disproved appears regularly in current literature.

[6] Newberry, *J. Chem. Soc.*, **107**, 855, 1520 (1915).

[7] See Jones and co-workers in *Am. Chem. J.* from 1900 onwards; *Carnegie Inst. Reports*, No. 80 (1907), No. 180 (1913), No. 230 (1915).

[8] Zelinski and Krapiwin, *Z. physik. Chem.*, **21**, 35 (1896); Serkoff, *J. Russ. Phys. Chem. Soc.*, **40**, 399 (1908); **41**, 1 (1909); **4**, 1921 (1910); Hägglund, *Arkiv. Kem. Min. Geol.*, **4**, No. 11, 1 (1911); Goldschmidt and co-workers, *Z. physik. Chem.*, **89**, 129 (1915); **91**, 46

ductance of such solutions is lower than that in pure alcohol, and in some cases the conductivity curve exhibits a minimum for a certain mixture which corresponds with the maximum viscosity.

In mixed solvents containing acetone [1] the relations are complex.

Goldschmidt (*loc. cit.*) found that addition of water to alcoholic hydrogen chloride, lithium chloride, sodium chloride, etc., depressed Λ_∞ rapidly at first, then more slowly as more water was added, until the water was present in $2\,n$ concentration, when the conductance increased on further addition. All acids which are slightly ionized in alcohol are affected in this way on addition of water.

The results of all investigators show that the effect of changing viscosity on mixing solvents is important in affecting the conductance, but no general conclusions can, apparently, be drawn. In acetone solutions, for example, no parallelism exists between conductance and viscosity curves,[2] whilst in solutions containing glycerol a marked parallelism was found.[3] In some cases, when the added non-electrolyte forms a stable complex with one of the ions, there is a decrease in viscosity.[4] When combination ceases, there may then be an increase in viscosity on further addition of non-electrolyte.[5]

(1916); *Z. Elektrochem.*, **19**, 226 (1913); **20**, 473 (1914); **22**, 11 (1916); Jones, Wightman, Davis and Holmes, *J. Chim. Phys.*, **12**, 385 (1914); Kremann and Brassert, *Monatsh.*, **31**, 195 (1910); Kreider and Jones, *Am. Chem. J.*, **45**, 282 (1911); Dorochevski and Dvorshontschik, *J. Russ. Phys. Chem. Soc.*, **46**, 1676 (1914); *C. A.*, **9**, 2173 (1915), who tested dilution formulæ of Lenz, *Beibl.*, **7**, 399 (1887), Arrhenius, *Z. physik. Chem.*, **9**, 487 (1892), and Wakeman, *ibid.*, **11**, 49 (1893), and found the equation $\Lambda = A - a/\sqrt[n]{v}$ to apply within narrow limits; Jones and Lindsay, *Am. Chem. J.*, **28**, 329 (1902); Whitman and Spencer, *J. Am. Chem. Soc.*, **50**, 1840 (1928).

[1] Serkoff, *loc. cit.;* Fischler, *Z. Elektrochem.*, **19**, 126 (1913); Jones and Mahin, *Am. Chem. J.*, **41**, 433 (1909); *Z. physik. Chem.*, **69**, 389 (1909); Davis, Hughes and Jones, *Z. physik. Chem.*, **85**, 513 (1913). Solutions containing glycerol: Pissarjewski and Shapovalenko, *J. Russ. Phys. Chem. Soc.*, **42**, 905 (1910); *C. A.*, **6**, 318 (1912); Guy and Jones, *Am. Chem. J.*, **46**, 131 (1911); Davis, Putnam and Jones, *Z. physik. Chem.*, **90**, 481 (1915). Formamide and alcohol: Davis and Johnson, *Carnegie Inst. Pub.*, **260**, 71 (1918). Pyridine and water: Ghosh, *J. Chem. Soc.*, **117**, 1390 (1920).

[2] Serkoff, *loc. cit.*

[3] Guy and Jones, *loc. cit.*

[4] Blanchard, *J. Am. Chem. Soc.*, **26**, 1315 (1904).

[5] Kraus, Electrically Conducting Systems, 1922, p. 119, who concludes that the conductance change is more nearly proportional to the fluidity change the smaller the molecules of the added non-electrolyte.

CHAPTER XII

THE ELECTROCHEMISTRY OF SOLUTIONS

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The study of the electromotive forces of galvanic cells of various types, which is so fundamental and necessary a part of electrochemistry, is itself to a very large extent a branch of the more general science of thermodynamics. Until it was realized that many of the fundamental phenomena of electrochemistry are subject to the exact methods of thermodynamics, little progress towards any real systematization of the subject could be effected.

The application of the exact methods of thermodynamics to this subject began with the studies of Helmholtz [1] and the earlier applications of the equation derived by Helmholtz.[2] which relates the electromotive force of a galvanic cell with the internal energy of a chemical reaction. Since the time of these studies, there has been a steady development of the subject which has led to a broader and more accurate knowledge of galvanic electromotive forces and the thermodynamics of solutions. Soon after the investigations of Helmholtz, Jahn and others, Nernst [3] developed his well-known osmotic theory and his formula for the concentration cell. These investigations made possible the definition of the normal electrode potential and gave a great impetus to the further development of the subject. Wilsmore [4] in 1900 compiled a table of standard normal electrode potentials, and in 1911 Abegg, Auerbach and Luther [5] collected all the data available up to that time. More recently G. N. Lewis and his colleagues, by employing more exact theoretical methods and attaining greater experimental precision, have increased the accuracy of the values of standard potentials to a very great extent.

The calculation of the variation of galvanic electromotive forces with the pressure, the temperature, and the concentration of the electrolyte, involves the general thermodynamics of solutions. The exact mathematical theory of this subject was first satisfactorily developed in the classic contributions of Gibbs.[6] Gibbs was concerned with fundamental mathematical considerations,

[1] Helmholtz, *Sitzungsber. der Berl. akad.* (1882); Ges. Abl., Bd. II.

[2] Czapski, *Wied. Ann.*, **21**, 203 (1884); Jahn, *Wied. Ann.*, **28**, 21 (1886); **28**, 491 (1886).

[3] *Z. physik. Chem.*, **2**, 613 (1888); **4**, 129 (1889).

[4] *Z. physik. Chem.*, **35**, 291 (1900).

[5] Messungen electromotorischer Kräfte galvanischer Ketten, *Abh. Deutschen Bunsen-Gesellschafft.*

[6] *Trans. of Connecticut Academy*, 1875–1878. Scientific Papers of J. Willard Gibbs, Vol. I, Longmans, Green and Co., 1906. The Collected Works of J. Willard Gibbs, Vol. I, Longmans, Green and Co., New York (1928).

and made no numerical calculations. Even after realization of the importance and usefulness of the "partial quantities" of Gibbs in the thermodynamics of solutions, the difficult task remains of devising methods by means of which partial quantities may be measured and employed in actual numerical calculations. This important step towards the application of the general equations to the specific problems of the physical chemistry of solutions has been carried out with consummate skill by G. N. Lewis [1] and his colleagues in this country, and by Brönsted and Bjerrum in Denmark. Further, the introduction by Lewis of the activity function has also gone far toward placing the thermodynamics of solution on a more exact basis, and toward making possible a more exact treatment of the galvanic cell and electrode potentials.

In the following discussion, the thermodynamics of galvanic cells in its relation to the general thermodynamics of aqueous solutions of both strong and weak electrolytes will be comprehensively treated. To achieve exactness and eliminate many of the difficulties accompanying the treatment of concentrated solutions, the activity function has been employed. For the sake of uniformity, the same nomenclature and symbols, conventions in regard to sign of electromotive force, etc., as employed by Lewis and Randall have been used.

Recently, the effects of the electrostatic fields of the ions upon their kinetic and thermodynamic properties have been investigated. This marks the beginning of a statistical theory of electrolytic solutions which so far has received its greatest impetus through the theory of Debye and Hückel.[2] With the development of statistical theory, we may expect ultimately to be able to compute the properties of solutions from the very fundamental ideas as to their inner nature, and not have to rely merely upon the purely macroscopic and external methods of thermodynamics. This theory and its applications will be considered as comprehensively as space will permit.

Following the discussion of reversible electromotive forces, and the thermodynamics of solutions of strong electrolytes, an introduction to the phenomena of electrolysis and polarization has been added. This may serve to bridge the gap from the exact study of reversible cells to the extended field of theoretical and applied electrochemistry.

The Galvanic Cell

Whenever two different phases are brought into contact, there may exist between them a difference in electrical potential. The potentials between two solid phases are employed in various kinds of thermocouples. Potentials exist between metals and gases, metals and solutions, at the boundary between two solutions which contain different electrolytes, or the same electrolyte at different concentrations, between a charged particle and the medium in which it is suspended. The cause, the magnitude and the nature of these contact differences of potential are very obscure. Their magnitude is a function of the constitution of the substances, their compositions, their physical states, the

[1] Lewis and Randall, Thermodynamics, McGraw-Hill Book Co., New York, (1923).
[2] *Physik. Z.*, **24**, 185 (1923).

temperature, the pressure and obscure surface conditions. The universality of the phenomenon makes the investigation of these potential differences a field of great importance.

The present discussion will be limited to a class of potential differences which are very closely associated with chemical reaction, and the properties of electrolytes in aqueous and non-aqueous solutions. We shall be concerned principally with combinations of three or more contact potential differences at surfaces between metal and solution, gas and solution, metallic solution and solution, two solutions, or metal and metal. Such combinations are designated galvanic cells. The absolute values of contact potential differences are not known. We must, therefore, rest content at the present time to consider them first in combination, and determine their values relative to some standard.

Of all possible combinations of this kind, there are two classes which should be differentiated. There are galvanic cells in which chemical reaction takes place even while no current is passing through the cell. A cell, similar to those constructed by Volta in 1800, and consisting of alternate zinc and copper plates between which was a fibrous material moistened with dilute sulphuric acid, evolves hydrogen when no current is flowing through the cell. Such a cell has but little value in the more exact development of the subject. Then, there is the more important class of cells in which no chemical reaction takes place until a current is caused to flow through them. The Weston cell, in which one electrode is a 12.5 per cent cadmium amalgam in contact with a saturated solution of cadmium sulphate containing crystals of $CdSO_4.\frac{8}{3}H_2O$, and the other electrode is mercury in the presence of solid mercurous sulphate, also in the saturated cadmium sulphate solution, remains in stable equilibrium at 25° [1] when there is no flow of electricity through it. The constancy of the electromotive force of such a cell depends on this stability, and unless the equilibrium in the cell is disturbed by electrolyzing or discharging, and thus producing chemical reactions, the electromotive force will remain constant.

Reversible and Irreversible Cells: A reversible process may be defined as a process of which every state is a condition of stable equilibrium. The evaporation of a given quantity of a liquid at constant temperature and at its vapor pressure, the isothermal expansion of a gas against a pressure exactly equal to the pressure of the gas are reversible processes. The criterion for reversibility is the state of equilibrium, and all measurements of reversible processes depend on the measurement of a system in equilibrium. All actual processes which take place in finite time, or which involve time as a variable, are irreversible.

The criterion of reversibility may now be applied to the galvanic cell.

In the first place, it is obvious that those cells in which there is chemical reaction when no current is flowing cannot be reversible, because an actual process is taking place, and such an unbalanced condition must be irreversible. The Weston cell, on the other hand, may,

[1] Recent investigations of Cohen and Moesveld, *Z. physik. Chem.*, **95**, 280 (1920); **104**, 403 (1923), have indicated the presence of a metastable or β modification of cadmium in the 12.5 per cent amalgam at temperatures under 23°, and have shown that the presence of this variety considerably changed the electromotive force of the cell at 0° and other low temperatures.

under certain conditions, be considered as a reversible cell. Imagine the electromotive force of the Weston cell exactly balanced by some outside electromotive force so that no chemical change is produced in it. Then, let this outside electromotive force be increased an infinitesimal amount. Reaction will be started in the Weston cell corresponding to some chemical change, and this reaction will be reversed if the outside electromotive force be diminished an infinitesimal amount. This would be an ideal condition of reversibility, and the exactly balanced state would require an infinitely sensitive galvanometer in the Weston cell circuit for its measurement. From these considerations, it is clear that any condition involving the passage of a finite current through the cell would be irreversible. In practice, the electromotive force of a cell is always measured by the method of balanced electromotive forces, or the potentiometer method, and the ideal condition, corresponding to reversibility, may be approached as more and more sensitive galvanometers are employed.[1]

Before passing to the consideration of reversible cells and their corresponding reactions, a few further important phenomena should be mentioned. In reversible cells, all substances involved must be in their most stable state. The presence of a metastable modification along with a stable modification of a substance would produce an electromotive force which would not correspond to a reversible process. Further, the potentials of metals depend to a very large extent on the physical structure and state of the metal. Metals in the crystalline form differ from finely divided metals, which are in the more stable physical state. It is well known that the physical state of metals deposited electrolytically is a function of various factors such as the acidity of the plating solution, and the current density employed during deposition, and that their potentials with respect to their ions vary accordingly. Apart from these considerations, there are phenomena which occur at boundary surfaces, and which influence the contact potentials. These phenomena, which include overvoltage and passivity, are, for the most part obscure, but constitute a very important branch of the science of general and technical electrochemistry. We shall reserve the consideration of these and polarization phenomena for a later section, and enter the more exact and fundamental field of reversible electromotive forces.

Reversible Cells and Chemical Reaction: It is important at this juncture to adopt a number of definite conventions for the designation of cells and the sign of electromotive force. The Weston cell will serve as an illustration, and will be written

$$\text{Cd (12.5 per cent amalg.)} \,|\, CdSO_4.\tfrac{8}{3}H_2O \,|\, CdSO_4 \text{ (sat)} \,|\, Hg_2SO_4 \,|\, \text{Hg; } \mathbf{E}_{25} = 1.01810,$$

where $\mathbf{E}_{25}$ denotes its electromotive force at 25° C. The vertical lines serve to divide the phases. When not evident, the nature of the phase, whether solid or liquid, will be denoted by (*s*) and (*l*), respectively. A gas and its pressure will be represented thus: H_2 (1 atm.), Cl_2 (1 atm.). When the phase is a solution, the molal concentration of the solution, expressed in mols (formula

[1] When measured by the potentiometer method, the electromotive force of a cell is equal to the algebraic sum of the contact differences of potential. We shall refer then to cell electromotive forces, potentials of electrodes in reference to some arbitrary standard electrode, and potential differences at contact surfaces.

weight) in 1,000 grams of solvent, will be given in brackets, and the saturated solution will be designated by (sat). The positive flow of electricity within this cell tends to take place from left to right. The chemical process corresponding to the cell is given by the equation

$$\text{Cd (12.5 per cent amalg.)} + \text{Hg}_2\text{SO}_4 + \tfrac{8}{3}\text{H}_2\text{O} = \text{CdSO}_4.\tfrac{8}{3}\text{H}_2\text{O}\ (s) + 2\text{Hg};\quad \mathbf{E}_{25} = 1.01810.$$

That is, the cell does electrical work when the reaction proceeds from left to right. The electromotive force, expressed in volts, will be taken as positive in the direction of the flow of positive current within the cell, or when negative flow is from right to left. The above electromotive force of the Weston cell will be employed as the standard.

When the electromotive force, **E**, is expressed in volts, it equals the electrical work in joules corresponding to the passage of one coulomb through the cell. If, in the cell reaction, **N** gram equivalents are changed, the total electrical work, corresponding to the passage of **NF** coulombs, will be **NEF**, where **F** is the Faraday, or 96,500 coulombs. Since the electromotive force of such a cell is measured under conditions which approach very closely true equilibrium states, **NEF** will be the reversible electrical work of the cell reaction in joules. In the above cell reaction, the value of **N** is 2.

Now, it is possible, by constructing different combinations, to obtain the reversible electrical work corresponding to the various types of chemical reactions. The common general classes are combination, displacement, oxidation, metathesis, and neutralization, and their corresponding reverse reactions.

The reaction of the cell

$$\text{Pt}\,|\,\text{H}_2\ (1\text{ atm.})\,|\,\text{HCl}\ (0.1)\,|\,\text{Cl}_2\ (1\text{ atm.})\,|\,\text{Pt};\quad \mathbf{E}_{25} = 1.4885$$

is

$$\tfrac{1}{2}\text{H}_2\ (g) + \tfrac{1}{2}\text{Cl}_2\ (g) = \text{HCl}\ (0.1),$$

which is illustrative of combination.

Many cells have been measured in which the chemical process is a displacement. These may be of various types, of which the Weston cell is a rather complicated example. A simpler cell [1] is

$$\text{Pt}\,|\,\text{H}_2\ (1\text{ atm.})\,|\,\text{HCl}\ (0.1)\,|\,\text{AgCl}\,|\,\text{Ag};\quad \mathbf{E}_{25} = 0.3522$$

and the corresponding cell reaction is

$$\tfrac{1}{2}\text{H}_2\ (1\text{ atm.}) + \text{AgCl}\ (s) = \text{Ag} + \text{HCl}\ (0.1).$$

If we had written for the cell reaction,

$$\text{H}_2\ (1\text{ atm.}) + 2\text{AgCl} = 2\text{Ag} + 2\text{HCl}\ (0.1),$$

which would correspond to the passage of two Faradays through the cell, the reversible electrical work would have been $2 \times 0.3522 \times 96{,}500$ or 67,975 joules.

[1] Noyes and Ellis, *J. Am. Chem. Soc.*, 39, 2532 (1917).

Another important type of cell representing a displacement reaction is the Daniell cell, or

$$\mathrm{Zn}\,|\,\mathrm{ZnSO_4}\ (1\mathrm{M})\,||\,\mathrm{CuSO_4}\ (1\mathrm{M})\,|\,\mathrm{Cu}.$$

The cell reaction in this case is

$$\mathrm{Zn} + \mathrm{CuSO_4}\ (1\mathrm{M}) = \mathrm{ZnSO_4}\ (1\mathrm{M}) + \mathrm{Cu}.$$

Actually, in this cell, there will be a junction between the zinc and copper sulphate solutions, and, at this boundary, there will be a potential difference which must be eliminated by some method before the potential of the cell reaction can be known. The elimination of this "liquid junction potential" from the total electromotive force of a cell will be indicated as above by introducing two vertical lines.

The following is a good example of a cell without a liquid junction in which the cell reaction is an oxidation. The reaction of the cell [1]

$$\mathrm{Hg}\,|\,\mathrm{HgCl}\,|\,\mathrm{KCl}\ (0.05),\ \mathrm{K_4Fe(CN)_6}\ (0.0005),\ \mathrm{K_3Fe(CN)_6}\ (0.0005)\,|\,\mathrm{Pt};\quad \mathbf{E} = 0.0609$$

is

$$\mathrm{Hg} + \mathrm{KCl}\ (0.05) + \mathrm{K_3Fe(CN)_6}\ (0.0005) = \mathrm{K_4Fe(CN)_6}\ (0.0005) + \mathrm{HgCl}\ (s).$$

In this cell, the solution is a mixture of three electrolytes. Commas are used merely for differentiating the electrolytes present. The cell

$$\mathrm{Pt}\,|\,\mathrm{SnCl_2}\ (0.1),\ \mathrm{SnCl_4}\ (0.1)\,||\,\mathrm{FeCl_2}\ (0.1),\ \mathrm{FeCl_3}\ (0.1)\,|\,\mathrm{Pt}$$

would correspond to the reaction

$$\mathrm{SnCl_2}\ (0.1) + 2\mathrm{FeCl_3}\ (0.1) = 2\mathrm{FeCl_2}\ (0.1) + \mathrm{SnCl_4}\ (0.1).$$

There is no example of a single cell without a liquid junction in which the reaction is a metathesis or double decomposition. However, Brönsted [2] by combining four cells has been able to determine the reversible electrical work of the reactions

$$\mathrm{NaCl}\ (s) + \mathrm{KBr.2H_2O} = \mathrm{KCl}\ (s) + \mathrm{NaBr.2H_2O},$$
$$\mathrm{KCl}\ (s) + \mathrm{NaClO_3}\ (s) = \mathrm{KClO_3}\ (s) + \mathrm{NaCl}\ (s),$$

where the compounds are all in the solid state.

The cell

$$\mathrm{Tl\ (amalg.)}\,|\,\mathrm{TlCNS}\ (s)\,|\,\mathrm{KCNS}\,||\,\mathrm{KCl}\,|\,\mathrm{TlCl}\ (s)\,|\,\mathrm{Tl\ (amalg.)},$$

which contains a liquid junction has been employed by Knüpffer [3] to measure the reversible electrical work of the reaction

$$\mathrm{TlCl}\ (s) + \mathrm{KCNS} = \mathrm{TlCNS}\ (s) + \mathrm{KCl}.$$

[1] Linhart, *J. Am. Chem. Soc.*, **39**, 615 (1917).
[2] *Det Kgl. Danske Videns. Selskab. Math.-fysis. Medd.*, No. 3 (1917).
[3] *Z. physik. Chem.*, **26**, 255 (1898).

Neutralization may be represented by the cell

$$Pt|H_2|OH^-\ (1M)||H^+\ (1M)|H_2|Pt;\quad E_{25} = 0.8280,$$

which corresponds to the reaction of the neutralization of strong acids and bases or

$$H^+\ (1M) + OH^-\ (1M) = H_2O\ (l).$$

These examples are sufficient to show that the electromotive forces corresponding to all the common types of reactions involving strong electrolytes may be obtained from suitable cells, or from combinations of suitable cells. Since we shall find that the reversible electrical work is a very important chemical quantity, the measurement of electromotive force of reversible cells constitutes a powerful method of investigating chemical reactions.

It should be emphasized that by far the most important consideration in dealing with galvanic cells is the exact knowledge of the cell reactions. Many errors have been made and many false conclusions drawn from measurements of electromotive forces without this knowledge.

The Fundamental Thermodynamics of the Galvanic Cell

The Thermodynamic Functions: The energy, U, the entropy, S, the work content, A, the heat content, H, and the free energy, F, are employed in general thermodynamics. In dealing with a particular problem of thermodynamics, it is sometimes more convenient to employ one function, sometimes another. The function employed depends on the nature of the constraints (fixed variables) to which the system under consideration is subjected. To avoid any subsequent confusion, it is desirable to discuss briefly these functions, their relation to the galvanic cell, and to introduce some fundamental equations which will be employed in succeeding deductions.

In the first place, the fundamental equation

$$dS = \frac{dU + pdV}{T}, \tag{1}$$

which Planck [1] has employed as a definition of the entropy of a body, will prove to be very convenient for many subsequent derivations. This equation measures the entropy change of a system in terms of its increase in internal energy and the work performed on another system. It defines the entropy of a system when p is the external pressure on the system when the system is in thermal equilibrium with its surroundings, or the pressure of the system, and, consequently, pdV is the work of a reversible process. In all actual or irreversible processes, where p' is the external pressure on the system when it is not in equilibrium with the surroundings,

$$dS > \frac{dU + p'dV}{T}. \tag{2}$$

These two equations express the content of the second law of thermodynamics. In the

[1] Planck, Treatise on Thermodynamics, Longmans, Green and Co. (1927). Translated by Ogg, p. 101.

case in which the system, that is, the body and its surroundings, is isolated, the familiar and very general expression of the second law

$$dS \geqq 0 \tag{3}$$

results. Thus, any irreversible change in an isolated system is accompanied by an increase in entropy of the system, while during any reversible change the variation in entropy is zero.

Consider any system as undergoing a reversible isothermal change and let w equal the work which this system is capable of doing during this change. It is an easy matter to imagine such a function that a change in it may be measured by the work done by the isothermal reversible process. In this case when the system passes from one state to another, this function, A, will change from a value A_1 to a value A_2, and

$$(A_1 - A_2) = (-\Delta A) = w.^1 \tag{4}$$

When the system does the reversible work, w, there will be a corresponding decrease in the value of A. For this reason, A may be regarded as the work content of the system.

Since w in the present case is the work of a reversible process, it is the maximum work obtainable from the change, and $(-\Delta A)$ will be independent of the path, and depend solely on the initial and final states of the system. The function A, like the energy and the entropy, is a single-valued function and depends solely on the variables of condition of the system. Further, A like U has no absolute value, but is always measured with respect to some normal state, arbitrarily chosen.

Although the above definition of A is useful, it is often very convenient to define it by an equation which possesses greater generality and which relates it to the energy and the entropy. Thus

$$A = U - TS. \tag{5}$$

is an analytical definition of A and is perfectly general.[2]

In cell processes, the total reversible work is the sum of the reversible electrical work, **NEF**, and the work gained by the expansion of the system under equilibrium conditions. Thus, for example, in the cell reaction at constant temperature and at constant pressure,

$$H_2\ (1\ atm.) + 2AgCl = 2HCl\ (0.1) + 2Ag,$$

there will be available the electrical work, **NEF**, but, at the same time, there will be a considerable contraction of volume $(-\Delta V)$, due, principally, to the disappearance of a mol of hydrogen. As a result, work corresponding to $p\Delta V$ will be done on the system. The total reversible work, w, will be **NEF** $+ p\Delta V$, where ΔV is the increase in volume.

Now, consider a function, F, which in general may be defined conveniently by the equation

$$F = A + pV, \tag{6}$$

where p is the pressure of the system and V is the total volume. At constant pressure, a finite change in F will be

$$\Delta F = \Delta A + p\Delta V = (-w) + p\Delta V.$$

Substituting in this equation **NEF** $+ p\Delta V$ for w, we find that

$$(-\Delta F) = \mathbf{NEF}. \tag{7}$$

[1] Δ denotes an increment.

[2] A is the Helmholtz free energy, or the Gibbs ψ function.

In all cell reactions, at constant pressure and temperature, a decrease in F may be obtained by measurement of the reversible electrical work. It is obvious, from the above considerations, that in cases of condensed systems where ΔV is very small, the change in A and the change in F may be nearly identical. Large errors may be made, however, in confusing these functions.

We shall later find it very convenient to employ the equation

$$F = U - TS + pV, \tag{8}$$

which defines the free energy, F.[1]

It is necessary further to consider one other very important function, the heat content, which may be defined by the equation

$$H = U + pV, \tag{9}$$

and which is related to F by

$$F = H - TS, \tag{10}$$

an equation similar to the one relating A and U.[2]

The heat content function is particularly important because in a chemical reaction carried out at constant pressure, ΔH equals the heat absorbed during the process, or the negative of the heat of reaction. According to the first law of thermodynamics,

$$q = \Delta U + p\Delta V,$$

when the work done is entirely caused by a change in volume, and where q is the heat absorbed. From equation (9) at constant pressure, it is seen that

$$\Delta H = \Delta U + p\Delta V.$$

When during a process the system absorbs heat, the heat of reaction has been ordinarily regarded as negative; it is clear therefore that, at constant pressure, ΔH is the negative of the heat of reaction. When ΔV is very small, ΔH and ΔU become nearly identical.

The variation of the heat content increment with the temperature is given by the well-known equation of Kirchhoff,[3]

$$\frac{\partial(\Delta H)}{\partial T} = \Delta C_p, \tag{11}$$

where ΔC_p is the difference between the sum of the heat capacities of the products and the sum of the heat capacities of the reactants at constant pressure.

The Equations of Gibbs and Helmholtz: The very important fundamental relations involving these functions and their temperature coefficients may readily be obtained from the equations which define them.

Thus, by differentiating (5), we obtain

$$dA = dU - TdS - SdT.$$

Substituting the value obtained for TdS from equation (1), we find

$$dA = -SdT - pdV,$$

whence, at constant volume,

$$\left[\frac{\partial A}{\partial T}\right]_v = -S.$$

[1] This is the Gibbs ζ function.

[2] H is the Gibbs χ function.

[3] *Ann. Physik*, (2) **103**, 177 (1858).

Substitution for the entropy in equation (5) gives

$$A = U + T\left[\frac{\partial A}{\partial T}\right]_v, \tag{12}$$

which is the important equation of Helmholtz. In precisely the same way, by differentiating (8), and substituting the value of TdS obtained from (1), we obtain

$$dF = -SdT + Vdp, \tag{13}$$

whence, at constant pressure,

$$\left[\frac{\partial F}{\partial T}\right]_p = -S.$$

Substituting this value in (10), we obtain

$$F = H + T\left[\frac{\partial F}{\partial T}\right]_p, \tag{14}$$

the extremely important fundamental equation of Gibbs.

The functions A, F, U and H do not possess absolute values but are measured in reference to some standard state. If we consider any change in a system which causes a finite variation of these functions, we write the Helmholtz and Gibbs equations

$$\Delta A = \Delta U + T\left[\frac{\partial(\Delta A)}{\partial T}\right]_v, \tag{15}$$

$$\Delta F = \Delta H + T\left[\frac{\partial(\Delta F)}{\partial T}\right]_p. \tag{16}$$

Of these equations, (14) and (16) are the most important and convenient in chemical calculations, since most measurements of chemical processes are carried out at constant pressure and temperature. In the following discussion, the free energy and heat content will be used exclusively. It will be understood, unless specifically mentioned, that we are dealing with processes at constant pressures, and the subscripts of the differential coefficients will be omitted.

Equations (14) and (16) are often employed for the convenience of calculation in the forms

$$\frac{\partial\left(\frac{F}{T}\right)}{\partial T} = -\frac{H}{T^2} \tag{17}$$

and

$$\frac{\partial\left(\frac{\Delta F}{T}\right)}{\partial T} = -\frac{\Delta H}{T^2}. \tag{18}$$

These equations along with (14) and (16) permit the important calculations of free energy and free energy increments from thermal data, and heat content from free energy data. Equations (17) and (18) form the basis for the calculation of the change in free energy with the temperature.

The Calculation of Free Energy and Heat Content Increments of Cell Reactions: When equation (16) is employed for the calculation of heat content changes from free energy data, it is customary to obtain the temperature coefficient of the free energy change, ΔF, by plotting ΔF against the temperature. From the slope of this curve at T, the temperature coefficient of the free energy change is read. By substituting this value and the value of ΔF in equation

(16), ΔH may readily be calculated. This method is more reliable in most cases than the method of determining the mean temperature coefficient of free energy over a larger temperature range in the neighborhood of T, since very often the free energy-temperature plot has a considerable curvature. By rearranging equation (16) and changing all signs, we obtain

$$(-\Delta H) = (-\Delta F) - T\frac{\partial(-\Delta F)}{\partial T}.$$

According to equation (7), $(-\Delta F)$ equals **NEF**, and, consequently,

$$(-\Delta H) = \mathbf{NEF} - \mathbf{NF}T\frac{\partial \mathbf{E}}{\partial T}. \qquad (19)^1$$

A comparison of values of $(-\Delta H)$ of a few cell reactions determined by measurement of electromotive force and by calorimetric measurement is given in the last two columns of Table I. The column headings make the table self-explanatory.

TABLE I

Comparison of Heat Content Decreases of Cell Reactions in Calories Determined by Measurements of Electromotive Force and by Thermochemical Measurements

Cell Reaction	E	$\frac{dE}{dT}$	$(-\Delta H)$ E.M.F.	$(-\Delta H)$ Thermochemical
(1) $Zn + 2AgCl = ZnCl_2$ (0.555M) $+ 2Ag$ (0° C.)	1.015	−0.000402	51989	52046
(2) $Pb + 2AgI = PbI_2 + 2Ag$ (25° C.)	0.21069	−0.000138	11610	11650
(3) $Cd + 2AgCl + 2{\cdot}5H_2O = CdCl_2.2.5H_2O + 2Ag$ (25° C.)	0.67531	−0.00065	40030	39530
(4) $Cd + PbCl_2 + 2{\cdot}5H_2O = CdCl_2.2{\cdot}5H_2O + Pb$ (25° C.)	0.18801	−0.00048	15250	14650

(1) Jahn, *Wied. Ann.*, **28**, 21 (1886).
(2) Taylor, *J. Am. Chem. Soc.*, **38**, 2295 (1916).
(3), (4) Taylor and Perrott, *ibid.*, **43**, 486 (1921).

In order to compute the heat content decrease accurately by means of the electromotive force method, the temperature coefficients of electromotive force must be obtained with great precision. Indeed, in the reactions in the above table, an error of 0.01 of a millivolt will cause an error of approximately 130 calories.

[1] In a system containing only liquids, solutions, and solids, $(-\Delta H)$ is nearly equal to $(-\Delta U)$ or the decrease in intrinsic energy. If the temperature coefficient of electromotive force is very small, equation (19) for a condensed system will approach $(-\Delta U) = \mathbf{NEF}$ and, if $(-\Delta U)$ is expressed in calories $\frac{(-\Delta U)}{23{,}074} = E$, which *inexact* expression is known as the Thomson rule.

Equation (18) may be employed for the calculation of a change in heat content from free energy data. The method is well illustrated by a calculation performed by Ellis [1] from electromotive force data of the cell

$$H_2\ (1\ \text{atm.})\,|\,HCl\ (c)\,|\,HgCl\,|\,Hg,$$

which corresponds to the cell reaction

$$H_2\ (1\ \text{atm.}) + 2HgCl = 2Hg + 2HCl\ (m).$$

Table II contains some of his electromotive force data.

TABLE II

ELECTROMOTIVE FORCE DATA OF THE CELL: H_2 (1 ATM.)|HCl (m)|HgCl|Hg

m	E.M.F.			$10^6\,\alpha$
	18°	25°	35°	
0.1004	0.39764	0.39884	0.40013	+ 386
0.3376	0.33845	0.33836	0.33794	− 75
0.7714	0.29654	0.29571	0.29411	− 460
4.484	0.15759	0.15506	0.15124	− 2384

The electromotive force **E** at different temperatures may be computed for each temperature by the equation

$$\mathbf{E} = \mathbf{E}_{25}(1 + \alpha(t - 25)),$$

where the values of α are given in the last column of the table. The free energy decrease of the cell reaction as written will equal $2 \times 23{,}074 \times \mathbf{E}$ calories, and also

$$(-\Delta F) = (-\Delta F)_{298}(1 + \alpha(T - 298)).$$

Now, if this value for $(-\Delta F)$ be substituted in (18) and the differentiation performed,

$$(-\Delta H)_{298} = (-\Delta F)_{298}(1 - 298\alpha)$$

TABLE III [2]

$(-\Delta F)$ AND $(-\Delta H)_{298}$ OF THE CELL REACTION IN CALORIES

m	$(-\Delta F)_{291}$	$(-\Delta F)_{298}$	$(-\Delta F)_{308}$	$(-\Delta H)_{298}$
0.1004	18351	18407	18466	16290
0.3376	15620	15616	15596	15965
0.7714	13685	13647	13593	15528
4.484	7273	7156	6980	12240

[1] *J. Am. Chem. Soc.*, **38**, 737 (1916).

[2] Usually in the text the centigrade temperature scale will be employed. In recording numerical data involving changes in the thermodynamic functions, it is more customary to employ the absolute temperatures.

is obtained. In Table III, are given values of $(-\Delta F)$ in calories computed from the electromotive forces, and $(-\Delta H)_{298}$ calculated by this last equation.

This method of calculation should be employed when it is possible to express the electromotive forces as a function of the temperatures by a simple equation.

Further Important Properties of the Free Energy: By differentiating (8) at constant temperature and pressure, we obtain

$$[\partial F]_{p,\,T} = dU - TdS + pdV.$$

But according to (1) and (2)

$$TdS \geqq dU + pdV,$$

whence by substitution

$$[\partial F]_{p,\,T} \leqq 0. \tag{20}$$

This equation corresponds to the statement that all actual variations in systems at constant temperature and pressure are accompanied by a decrease in free energy, and that the criterion for stable equilibrium is that the free energy remains unchanged. This very important principle can be clearly understood by further consideration of the cell reactions. When the cell reaction can proceed spontaneously, in a direction corresponding to the direction of the flow of positive electricity in the cell, there will be a decrease in free energy. It is then obvious that, at constant temperature and pressure, a cell reaction can only proceed in a direction corresponding to a decrease in F, or when $\Delta F < 0$. The sign of the free energy change is thus an exact criterion for predicting the direction of the reaction. The determining factor of stable equilibrium of the cell reaction will then be the condition that at constant temperature and pressure

$$\Delta F = 0, \tag{21}$$

a relation directly deducible from equation (13). The value of the free energy is thus not only a criterion of equilibrium but also of the stability of systems. For, if we consider the reaction

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 = HCl\ (0.1); \qquad \Delta F_{298} = -34{,}346, \qquad \text{or} \qquad (-\Delta F)_{298} = 34{,}346,$$

we find that the change from left to right is accompanied by a very large decrease in free energy. It may be said that the system hydrogen and chlorine gas is very unstable. The decrease in free energy may therefore be considered as a measure of the affinity of a reaction, and in many systems of thermodynamics $(-\Delta F)$ has been denoted the "affinity."

The Concentration Cell without Liquid Junction: Up to the present, only the free energy and heat content changes of cell reactions, which are complete chemical reactions and which do not involve changes in composition of any of the phases, have been discussed. We have now to consider free energy and heat content changes of quite a different nature, and processes in which the compositions of the phases play a predominant rôle.

The electromotive forces of cells, corresponding to the following cell reactions, measured by Linhart,[1] will serve as an illustration:

$$\tfrac{1}{2}H_2\ (1\ \text{atm.}) + AgCl = Ag + HCl\ (0.001);$$
$$E_{25} = 0.5785; \quad (-\Delta F)_{298} = 55{,}822$$

and

$$\tfrac{1}{2}H_2\ (1\ \text{atm.}) + AgCl = Ag + HCl\ (0.0483);$$
$$E_{25} = 0.3870; \quad (-\Delta F)_{298} = 37{,}34$$

[1] Linhart, *J. Am. Chem. Soc.*, **41**, 1175 (1919).

If the second reaction be subtracted from the first, the result will be

$$\text{HCl (0.0483)} = \text{HCl (0.001)}; \quad \mathbf{E}_{25} = 0.1915; \quad (-\Delta\overline{F})_{298} = 18{,}479.$$

The free energy decrease is in joules. This equation means that the net effect of the two cell reactions is the reversible transfer of a mol of hydrochloric acid from a solution of 0.0483 molal concentration to a solution of 0.001 molal concentration, and that the free energy decrease of such a change is 18,479 joules. In other words, $(-\Delta\overline{F})$ is the free energy decrease when a mol of hydrochloric acid disappears at 0.0483 molal concentration and appears at 0.001 molal concentration. The most important point is that $(-\Delta\overline{F})$ may be regarded as the difference of two quantities, which are the change in free energy, $\overline{F}_2$, when a mol of hydrochloric is added to an infinitely large quantity of 0.0483 molal concentration, and the change in free energy, $\overline{F}_1$, when a mol is added to an infinitely large quantity of solution containing 0.001 molal hydrochloric acid. $\overline{F}_2$ and $\overline{F}_1$[1] will denote the partial molal free energies of the hydrochloric acid in the two solutions respectively. It is always the case that the partial free energy is greater in the more concentrated solution, or $\overline{F}_2$ is greater than $\overline{F}_1$. Consider the transfer of a mol from the more concentrated to the more dilute solution. The *removal* of this mol from the concentrated solution will be accompanied by a change in free energy equal to $-\overline{F}_2$, and the addition of this mol to the more dilute solution will be accompanied by a change in free energy $+\overline{F}_1$. The total free energy increment of transfer will be the sum of these quantities, $(\overline{F}_1 - \overline{F}_2)$ or $-(\overline{F}_2 - \overline{F}_1)$, which in the present case equals a decrease in free energy $(-\Delta\overline{F})$.

In a similar manner, by subtracting the values of the heat content changes of the cell reactions computed by the Gibbs-Helmholtz equation (Table III) at two different concentrations, the difference in partial molal heat contents of the acid at the two concentrations may be obtained. From the nature of these processes we are led to the consideration of a whole group of quantities which will prove to be of great importance in the application of thermodynamics to solutions.

These changes in partial molal free energy and heat content could have been obtained directly from measurements of cells of the type

$$\text{Ag}\,|\,\text{AgCl}\,|\,\text{HCl}\ (m_2)\,|\,\text{H}_2\,|\,\text{HCl}\ (m_1)\,|\,\text{AgCl}\,|\,\text{Ag},$$

where the net result of the cell reaction would be the change

$$\text{HCl}\ (m_2) = \text{HCl}\ (m_1).$$

This type of cell will be denoted the concentration cell without liquid junction.

For the measurement of partial free energy changes of electrolytes containing a metal which readily reacts with water, there are available cells in which the metal electrode is a very dilute amalgam. For example, the cell

$$\text{Ag}\,|\,\text{AgCl}\,|\,\text{KCl}\ (m_2)\,|\,\text{K (dil. amalg.)}\,|\,\text{KCl}\ (m_1)\,|\,\text{AgCl}\,|\,\text{Ag}$$

[1] A partial quantity or a change in a partial quantity will always be represented by a dash over the symbol.

affords measurement of the partial free energy change corresponding to the transfer

$$KCl\ (m_2) = KCl\ (m_1).$$

The determination of partial free energy and heat content changes by the electromotive force method may also be applied to the study of solutions of electrolytes in metallic solvents. The electromotive force of the cell at constant pressure and temperature

$$Me\ (m_2)\ (amalg.)\,|\,MeX\ (solution)\,|\,Me\ (m_1)\ (amalg.),$$

consisting of two amalgam electrodes at different concentrations connected by a solution of a salt of the metal, MeX, is independent of the concentration of this salt solution and depends only on the composition of the amalgam. The net effect of the cell reaction is the disappearance of the metal from the amalgam of the higher concentration, and its appearance in an amalgam of lower concentration. This process is accompanied by a decrease in free energy equal to the difference in partial free energies of the metal in the amalgams of the two concentrations, or $-(\overline{F}_2 - \overline{F}_1)$ if m_2 is greater than m_1. A most exhaustive study of the cell

$$Tl\ (m_2)\ (amalg.)\,|\,Tl_2SO_4\,|\,Tl\ (m_1)\ (amalg.)$$

has been carried out by Richards and Daniels,[1] as a result of which the partial free energy and heat content changes of both the thallium and mercury are accurately known.[2] Indeed, the stability of the amalgams permitted measurements to solutions as concentrated as 40 per cent of thallium.

This type of cell has been mentioned to illustrate that electromotive force measurements are of great value in the study of metallic solutions. Since the present discussion is confined particularly to solutions of electrolytes, further discussion of this interesting subject will be omitted.

Partial Molal Quantities

General Considerations: The value of a thermodynamic function, for example, the energy, of a simple substance of one component in a given state in reference to some standard state is determined by the variables of condition, the pressure, the volume and the temperature. Thus,

$$U = f(p, v, T) + U_0,$$

where U_0 is a normal state, arbitrarily selected. There is always some relation, such as

$$f(p, v, T) = 0,$$

[1] *J. Am. Chem. Soc.*, **41**, 1732 (1919).

[2] Lewis and Randall, *J. Am. Chem. Soc.*, **43**, 233 (1921).

which is called an equation of state of the substance, and as a result of which one of the variables depends on the other two. It is then possible to evaluate the function by means of any two independent variables. Thus,

$$U = f(v, T) + U_0 = f(p, T) + U_0, \text{ etc.},$$

is true for any simple substance.

A thermodynamic function of a phase composed of two or more components is not determined by two of the above independent variables, but is only determined by two of these variables and the masses of the components. We shall find it most convenient to choose the pressure and temperature as well as the masses as the independent variables. The energy of a given phase may be expressed by

$$U = f(p, T, m_1, m_2, \cdots m_c) + U_0.$$

In like manner the general equation for the free energy of the phase is

$$F = f(p, T, m_1, m_2, \cdots m_c) + F_0,$$

where m_1, m_2, etc., are the masses of the c components of the phase, and F_0 is the free energy of an arbitrarily selected state. If we now consider an infinitesimal change in F and partially differentiate the right-hand member of this equation, we obtain

$$dF = \frac{\partial F}{\partial p} dp + \frac{\partial F}{\partial T} dT + \frac{\partial F}{\partial m_1} dm_1 + \frac{\partial F}{\partial m_2} dm_2 + \cdots \frac{\partial F}{\partial m_c} dm_c.$$

But, according to equation (13),

$$\partial F = - SdT + vdp$$

for a phase, or a system of phases at constant composition, and, therefore,

$$dF = - SdT + vdp + \frac{\partial F}{\partial m_1} dm_1 + \frac{\partial F}{\partial m_2} dm_2 + \cdots \frac{\partial F}{\partial m_c} dm_c. \qquad (22)$$

In general, we shall make these partial derivatives in respect to mass equal to μ_1, μ_2, etc., respectively, according to the notation of Gibbs, and, as a consequence, equation (22) becomes

$$dF = - SdT + vdp + \mu_1 dm_1 + \mu_2 dm_2 + \cdots \mu_c dm_c \qquad (23)$$

and, at constant pressure and temperature,

$$dF = \mu_1 \partial m_1 + \mu_2 \partial m_2 + \cdots \mu_c \partial m_c. \qquad (24)$$

Equation (23), which was originally obtained by Gibbs, and relations immediately deducible from it, may serve as a general fundamental relation underlying the thermodynamics of solutions.[1] This equation is valid for any phase of a c component system. By considering a system of P phases, and by using an

[1] See van der Waals-Kohnstamm, Lehrbuch der Thermodynamik, Vol. II (Maas and van Suchtelen, Amsterdam).

equation similar to this but involving the energy, Gibbs [1] in his famous memoir was able to deduce the phase rule. It should always be borne in mind that equation (23) and similar ones make possible an exact study of systems of many components in one phase, or many phases. In considering complicated chemical systems, there is no safer method than to employ these general equations of Gibbs.[2] An important conclusion for the discussion in hand is the principle, immediately deducible upon application of equation (23) to a system of phases, that when a polycomponent system in p phases is in stable equilibrium, and, if μ_1, μ_1', $\cdots$, μ_1^p represent the μ values of the first component, μ_2, μ_2', $\cdots$, μ_2^p represent the μ values of the second component throughout the p phases, etc., for the c components, then, at constant pressure and temperature,

$$\left.\begin{aligned} \mu_1 &= \mu_1' = \mu_1'' \cdots = \mu_1^p, \\ \mu_2 &= \mu_2' = \mu_2'' \cdots = \mu_2^p, \text{ etc.} \end{aligned}\right\} \tag{25}$$

It was because of this property of these partial derivatives that Gibbs denoted them the "chemical potentials."

Like the entropy or energy, the free energy of a homogeneous system is doubled if its mass is doubled. From this property, and from inspection of equation (23), it is clear that μ_1, μ_2, etc., are independent of the masses, and depend only on the composition, or relative quantities of the components, and the units in which the free energy and masses are expressed. As a consequence, equations (23) or (24) may be integrated term by term. Equation (24) thus becomes

$$F = \mu_1 m_1 + \mu_2 m_2 + \cdots + \mu_c m_c. \tag{26}$$

Complete differentiation of this latter equation gives

$$dF = \mu_1 \partial m_1 + m_1 \partial \mu_1 + \mu_2 \partial m_2 + m_2 \partial \mu_2 + \cdots \mu_c \partial m_c + m_c \partial \mu_c. \tag{27}$$

Elimination of dF from (24) and (27) gives the important equation

$$m_1 \partial \mu_1 + m_2 \partial \mu_2 + \cdots m_c \partial \mu_c = 0. \tag{28}$$

We have yet to consider the units in which these quantities may be expressed, and, for the sake of simplicity, let us choose a phase of two components. If (26) is divided by $(m_1 + m_2)$ or the total mass, we obtain

$$\frac{F}{(m_1 + m_2)} = \left(\frac{m_1}{m_1 + m_2}\right)\mu_1 + \left(\frac{m_2}{m_1 + m_2}\right)\mu_2.$$

Thus, if $\dfrac{F}{m_2 + m_1}$ is the free energy per gram, $\left(\dfrac{m_1}{m_1 + m_2}\right)$ and $\left(\dfrac{m_2}{m_1 + m_2}\right)$ are the weight fractions of the components, and μ_1, μ_2 or $\dfrac{\partial F}{\partial m_1}$, $\dfrac{\partial F}{\partial m_2}$ may be denoted

[1] Transactions of the Connecticut Academy (1875–1878). Scientific Papers of Willard Gibbs, Vol. 1. Longmans and Co.

[2] Williamson and Morey, *J. Am. Chem. Soc.*, **40**, 49 (1917); Morey and Williamson, *J. Am. Chem. Soc.*, **40**, 59 (1917); Morey, *J. Franklin Inst.*, **194**, 425 (1922).

partial specific free energies. In a similar manner, the free energy per mol of a phase may be defined by $\frac{F}{n_1 + n_2}$, where n_1 and n_2 are the number of mols of each component, respectively. Substituting mols for grams, we obtain according to (26)

$$\frac{F}{n_1 + n_2} = \frac{n_1}{n_1 + n_2}\overline{F}_1 + \frac{n_2}{n_1 + n_2}\overline{F}_2,$$

where μ_1 and μ_2 are now $\overline{F}_1$ and $\overline{F}_2$, the partial molal free energies, and $\frac{n_1}{n_1 + n_2}$ and $\frac{n_2}{n_1 + n_2}$, which we denote N_1 and N_2, are the mol fractions.

Thus, denoting the free energy per mol, F, we may write (26) and (28)

$$F = N_1\overline{F}_1 + N_2\overline{F}_2 + \cdots + N_c\overline{F}_c \tag{29}$$

and

$$o = N_1\partial\overline{F}_1 + N_2\partial\overline{F}_2 + \cdots N_c\partial\overline{F}_c. \tag{30}$$

Now, in the same manner, it is possible to regard many quantities such as the heat content, the volume, the entropy, the heat capacity, etc., as functions of the masses only when the pressure and temperature of the system are constant, and, consequently, the same general method of partial differentiation may be applied. In general, if we let G equal the value of the property of 1 mol of the whole phase, we have the following three fundamental and useful equations of partial molal quantities, namely,

$$d\,G = \overline{G}_1\partial N_1 + \overline{G}_2\partial N_2 + \cdots + \overline{G}_c\partial N_c, \tag{31}$$

$$G = \overline{G}_1 N_1 + \overline{G}_2 N_2 + \cdots + \overline{G}_c N_c, \tag{32}$$

$$o = N_1\partial\overline{G}_1 + N_2\partial\overline{G}_2 + \cdots + N_c\partial\overline{G}_c. \tag{33}$$

By the use of the general thermodynamic equations of Gibbs and the consideration of units, we are thus brought into contact with a class of quantities which are of utmost importance in the thermodynamics of solutions. The development of this subject since the time of Gibbs, and, particularly, the methods of employing the partial molal quantities in numerical calculations have been brought about very largely by the researches of Lewis and his colleagues.[1] In the present discussion, some of their methods will be employed as the occasion may arise, but no attempt will be made to give a comprehensive treatment of the subject.

The Direct Determination of Partial Molal Heat Content from Calorimetric Data: The physical significance of partial quantities may be clearly understood

[1] These investigations have been revised and corrected and a very comprehensive treatment of the subject has been presented by Lewis and Randall, Thermodynamics. McGraw-Hill Book Co. (1923).

by considering the heat of dilution by water of a salt solution of a given concentration. We may employ for this purpose the data of Stearn and Smith [1] on the heat of dilution of a 2.9 molal strontium chloride solution by different quantities of water. The results which are given in Table IV were carried out at 25° and 1 atmosphere. If the heat of dilution is positive, the system evolves heat as a result of the change, and, consequently, there will be a decrease in heat content or vice versa.

TABLE IV

HEAT CONTENT DECREASE, AND MOLAL HEAT CONTENT DECREASE OF A 2.9M STRONTIUM CHLORIDE ON DILUTION BY DIFFERENT QUANTITIES OF WATER

Δn_1	$(-\Delta H)$	$\frac{(-\Delta H)}{\Delta n_1}$
Water of Dilution (Mols.)	Total Heat of Dilution (Cals.)	Mean Heat Content Decrease per Mol. (Cals.)
37.2	129.8	3.49
30.0	112.4	3.75
30.0	114.1	3.80
27.7	109.2	3.95
20.0	86.3	4.31
19.5	85.4	4.38
10.0	48.5	4.85

In Fig. 1, the values of $\frac{(-\Delta H)}{\Delta n_1}$ are plotted against the number of mols of water added. This plot is a straight line and, consequently, the results may be extrapolated to zero Δn_1. It is thus found that $\frac{(-\Delta H)}{\Delta n_1}$ equals 5.4 when Δn_1 equals zero. This is exactly the definition of the derivative of $-H$ with respect to n_1, and, since it refers to the heat content change produced by one of the components while the mass of the other component is constant, it equals the negative of $\frac{\partial H}{\partial n_1}$, or $\overline{H}_1$, the partial molal heat content of the component water. Or, we may equally well say that $\overline{H}_1$ equals the change of heat content of an infinitely large quantity of the solution on the addition of a mol of water.

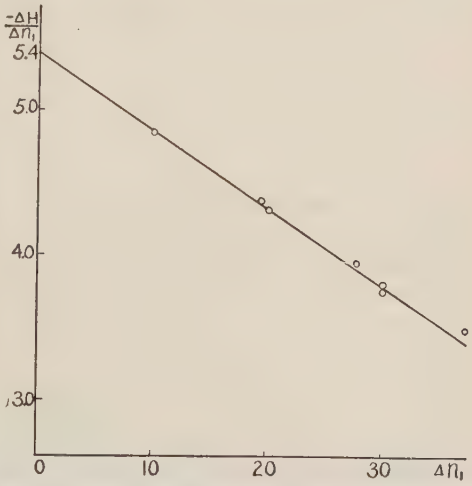

FIG. 1. Molal Heat Content Decrease of Strontium Chloride

[1] *J. Am. Chem. Soc.*, **42**, 18 (1920).

By a series of measurements of this kind, Stearn and Smith have obtained the partial molal heat content of water in strontium chloride solutions of different concentrations. In tabulating a partial molal quantity, it is necessary to refer its value to another standard state. It is convenient to employ as a standard state an infinitely dilute solution of an electrolyte. Thus, for a change in a partial molal quantity of the water or strontium chloride in the above solution, we would have $(\overline{G}_1 - \overline{G}_1^0)$ and $(\overline{G}_2 - \overline{G}_2^0)$, respectively. In all the subsequent discussion the subscript 1 will refer to the water, and the subscript 2 to the electrolyte. The partial molal quantity of the solvent in pure solvent, or $\overline{G}_1^0$, is zero and, consequently, this case is very simple. Following throughout the notation of Lewis and Randall, we shall let these differences of partial heat contents equal $\overline{L}_1$, $\overline{L}_2$, respectively, and call these quantities the relative partial molal heat contents. In Table V, the data of Stearn and Smith on the relative partial heat contents of water at different molal concentrations of strontium chloride are given.

TABLE V

Relative Partial Molal Heat Contents of Water in Strontium Chloride Solutions at 25°

c	$\overline{L}_1$
0	0.00
0.20	− 0.25
0.425	− 0.50
0.80	− 0.62
1.20	− 0.90
1.55	− 1.11
2.00	− 1.75
2.4	− 2.10
2.9	− 5.40
3.2	− 7.20

Relative Partial Molal Heat Content of Hydrochloric Acid from Electromotive Force Data: In an earlier section, it was shown that, from electromotive force measurements, it was possible to obtain the free energy change accompanying the transfer of a mol of hydrochloric acid from a solution of one concentration to a solution of another concentration. It was also shown that this change could be regarded as the difference of two quantities, which are the free energy changes on adding a mol to very large quantities of the solutions, respectively. It is clear now that these quantities are really the partial derivatives of the free energies with respect to the number of mols of the component in question, and that the electromotive force method measures the partial molal free energy change of the component transferred by the cell reaction. Further, by measuring the temperature coefficients of these cells, it was also found possible to compute the differences in partial molal heat contents of the electrolyte transferred. We shall now confine our attention more closely to the properties of these quantities, and consider the partial molal heat

content and free energy of hydrochloric acid obtained from the data of Ellis[1] and Noyes and Ellis.[2]

In Table VI, their data on the decreases in heat content of transfer in joules at 25° of a mol of hydrochloric acid from a solution of concentration m to a concentration 0.1 molal have been compiled.

TABLE VI

DECREASE IN HEAT CONTENT AND FREE ENERGY WHEN 1 MOL OF HYDROCHLORIC ACID IS TRANSFERRED FROM m TO 0.100M AT 25°

m	$(-\Delta\overline{H})$	$(-\Delta\overline{F})$
4.484	8474	23544
1.928	3591	15744
1.038	1937	11679
0.771	1619	9971
0.509	999	7757
0.338	260	5856
0.1	0	0
0.0332	− 435	− 5138
0.00948	− 745	− 11044
0.00338	− 915	− 15898
0.000999	− 930	− 21878
0	− 1050 (extrapolated)	− ∞

It is important to note from these data that $(-\Delta\overline{F})$ approaches $-\infty$ as m approaches zero, and that this behavior is quite different from the variation of $(-\Delta\overline{H})$ with the concentration. We shall reserve the discussion of the partial molal free energy for a later section and devote our attention to the partial molal heat content change. In Fig. 2 have been plotted the values of $(-\Delta\overline{H})$ and $m^{1/2}$ at the lower concentrations. This curve is a straight line and, consequently, may be extrapolated to zero concentration. This extrapolated value is − 1050. Assigning in the customary way the value $\overline{H}_2^0$ for the partial heat content of the acid at zero concentration, the values of $\overline{L}_2$ or $(\overline{H}_2 - \overline{H}_2^0)$ at round concentrations have been read off a plot of the results in Table VI. These results have been converted to calories by dividing by 4.182 and are given in the fourth column of Table VII.

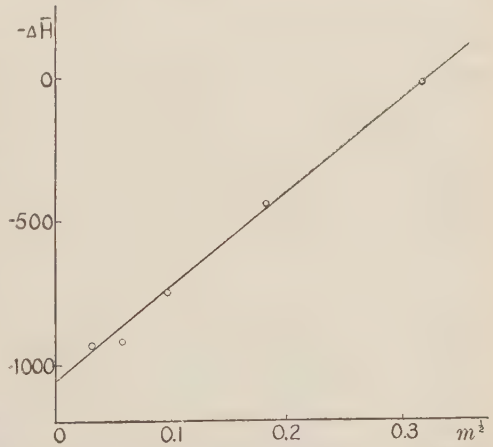

FIG. 2. Molal Heat Content Decrease of Hydrochloric Acid

The Calculation of a Relative Partial Molal Heat Content of Water from the Relative Partial Heat Content of Hydrochloric Acid: According to

[1] Ellis, *J. Am. Chem. Soc.*, **38**, 737 (1916).

[2] *J. Am. Chem. Soc.*, **39**, 2532 (1917). The cells employed by these investigators have been considered in an earlier section.

equation (32),

$$H = N_1\overline{H}_1 + N_2\overline{H}_2 \tag{34}$$

and

$$H_0 = N_1\overline{H}_1^0 + N_2\overline{H}_2^0, \tag{35}$$

whence L, the total relative heat content, $(H - H_0)$, will be

$$L = N_1\overline{L}_1 + N_2\overline{L}_2. \tag{36}$$

Further, according to (33),

$$o = N_1\partial\overline{L}_1 + N_2\partial\overline{L}_2. \tag{37}$$

By means of this latter equation, it is possible to determine the value of the relative partial molal heat content of one component when that of the other component is known. For example, by rearranging and integrating (37), the relative partial molal heat content, $\overline{L}_1$, of the water in the hydrochloric acid solutions will be given by

$$\overline{L}_1 = -\int \frac{N_2}{N_1}\partial\overline{L}_2. \tag{38}$$

$\overline{L}_1$ will equal the negative of the integral of the right-hand member, which expression may be easily evaluated by a graphical method. Fig. 3 contains a plot of $\frac{N_2}{N_1}$ against $\overline{L}_2$, the relative partial molal heat content of the acid. At a given concentration, or value of $\frac{N_2}{N_1}$, the area under this curve from 0 to $\frac{N_2}{N_1}$ equals this integral, and also the negative of $\overline{L}_1$. This area was easily evaluated from the plot by counting squares. The results obtained are compiled at round concentrations in the third column of Table VII. In the fifth and sixth columns of this table, for the sake of comparison, are also included $\overline{L}_1$, the relative partial molal heat content of water in aqueous sodium chloride solutions, and $\overline{L}_2$, the relative partial molal heat content of sodium chloride in the same solutions. These were obtained at the designated concentrations from a curve of the results of Lewis and Randall.[1]

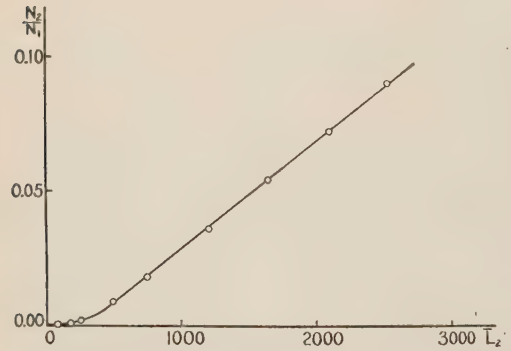

Fig. 3. Relative Partial Molal Heat Content of Hydrochloric Acid

[1] Thermodynamics, Chapter VIII, Table 5. The experimental data employed were obtained by Randall and Bisson, *J. Am. Chem. Soc.*, **42**, 347 (1920).

TABLE VII

RELATIVE PARTIAL MOLAL HEAT CONTENTS (IN CALORIES) OF HYDROCHLORIC ACID AND WATER IN HYDROCHLORIC ACID SOLUTIONS AND SODIUM CHLORIDE AND WATER IN SODIUM CHLORIDE SOLUTIONS

m	$\frac{N_2}{N_1}$	HCl		NaCl	
		$\bar{L}_1$	$\bar{L}_2$	$\bar{L}_1$	$\bar{L}_2$
0	0	0	0	0	0
0.001	0.000018	—	25.1	—	—
0.01	0.00018	− 0.012	78.9	0.01	− 1
0.05	0.0009	− 0.052	177	0.03	− 3
0.1	0.0018	− 0.161	251	0.05	− 8
0.5	0.009	− 1.16	496	0.65	− 120
1	0.018	− 3.66	747	3.4	− 332
2	0.036	− 15.8	1206	10.0	− 564
3	0.054	− 37.7	1651	17.4	− 736
4	0.072	− 66.6	2103	21.9	− 810
5	0.09	− 103.6	2541	19.4	− 779

It is important to note that $\bar{L}_1$ is negative in hydrochloric acid solutions and positive in sodium chloride solution s,and that $\bar{L}_2$ is positive in hydrochloric acid solutions and negative in sodium chloride solutions.

The Partial Molal Free Energy and Concentration of an Electrolyte: In the above discussion, it was found that the partial molal heat contents of both the water and the electrolyte in the two component solutions approached a limiting value as the concentration approached zero. The behavior of the partial free energy is quite different. To illustrate this, we plot in Fig. 4 the typical values of $(-\Delta\bar{F})_{298}$ of a uniunivalent electrolyte obtained from Table VI against the logarithm of the concentration. The resulting curve approaches a straight line as m decreases. The limiting value of the slope of this curve as m approaches 0 is 2×5708.1 joules. If the natural logarithm of the concentration had been plotted, this slope would be equal to 2×2479.0 joules, which in turn is equal to

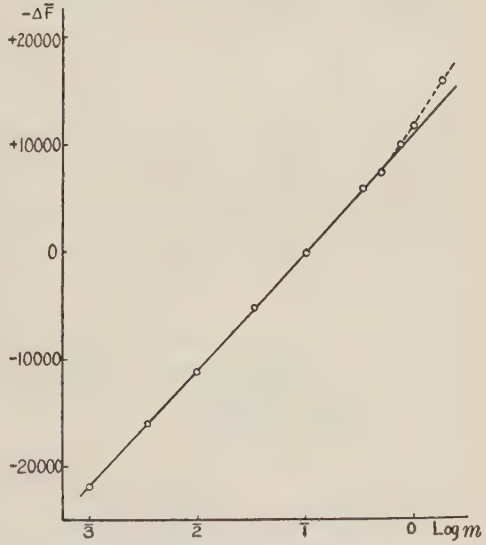

FIG. 4. Molal Free Energy of Hydrochloric Acid

$2 \times RT$, where R is the gas constant in joules, and T is the absolute temperature, or 298.1. Thus, as a law, only to be regarded as exactly valid in infinitely dilute solution, for the relative partial free energy of a uniunivalent electrolyte at constant temperature, we have

$$\overline{F} - \overline{F}_0 = 2RTlnm + I, \tag{39}$$

where I is a constant and is a function of an arbitrary standard state, $\overline{F}_0$. This equation will be equally valid for any uniunivalent electrolyte, and at any temperature, providing the partial free energy differences are measured at constant temperature. Similarly for a biunivalent or a triunivalent salt in very dilute solutions, we obtain

$$\overline{F} - \overline{F}_0 = 3RTlnm + I$$

and

$$\overline{F} - \overline{F}_0 = 4RTlnm + I, \tag{39a}$$

respectively. Since all electrolytes approach complete dissociation as their concentration approaches zero, the range of validity of these equations would probably be extended if the true ion concentration were employed, instead of the molal concentration, m. Upon differentiation, we would obtain for any electrolyte

$$\partial\overline{F} = \nu RT\partial lnm_{\pm}, \tag{40}$$

where ν is the sum of the number of anions and cations formed by dissociation and $m_{\pm}$ is the true degree of dissociation times m. For a change in partial free energy in very dilute solutions between two concentrations, it is obvious that

$$\overline{F}_2 - \overline{F}_1 = \nu RTln\frac{m_{\pm}''}{m_{\pm}'}. \tag{41}$$

The partial free energy is greater in the solution of higher concentration, and thus a transfer from a higher to a lower concentration, or from $m_{\pm}''$ to $m_{\pm}'$, is accompanied by a decrease in free energy. It will be shown in the subsequent discussion that (40) and (41) are particular expressions of a more general limiting law which includes gases, undissociated solutes and ions.

As a result of these considerations, it follows that the partial molal free energy becomes $-\infty$ at zero concentration, and, for this reason, special methods, not required in calculating partial molal heat contents, are necessary in calculating the partial free energies. We are thus led to the consideration of another thermodynamic function which will be shown to be very useful in subsequent calculations.

The Activity Function

In two papers, G. N. Lewis[1] introduced two new functions, the fugacity and the activity, into thermodynamic chemistry. In these papers these functions were defined, nearly all of their important relations with the other thermody-

[1] *Proc. Am. Acad.*, **37**, 45 (1901); **43**, 259 (1907).

namic functions and the variables of condition were deduced, and their usefulness predicted. Since the first of these papers, and, particularly, since 1912, a large literature on this subject has developed, which is devoted principally to studies of the activities of electrolytes and ions in aqueous solutions. A most comprehensive calculation and discussion of this recent work has been made by Lewis and Randall.[1]

In his first papers, Lewis developed the thermodynamics of the fugacity and activity functions from some fundamental definitions, and the laws of thermodynamics, by a cyclic method. This laborious method has now been abandoned, and a mathematically simpler development, using the thermodynamic functions, has been adopted. We shall employ the latter, for, aside from its simplicity, it conforms well with the recent methods of treatment of Brönsted,[2] Bjerrum[3] and others. Since the activity has been used exclusively in the study of solutions of electrolytes, we shall simplify the present treatment of the subject by omitting any consideration of the fugacity.[4]

Before proceeding to the discussion, it should be understood that these useful functions have been introduced in order to simplify and render exact many complicated thermodynamic calculations. Their introduction adds nothing new to the content of thermodynamic theory, and they are not so important as the more fundamental functions such as the entropy and free energy.

Definition of Activity: A convenient method of defining the activity of a component of a system is by the equation

$$F = RTln\xi + i, \tag{42}$$

where ξ is the activity in general and i is a constant.

The free energy has no absolute value and, consequently, is measured in reference to some standard state, F_0. Thus

$$F - F_0 = RTln\frac{\xi}{\xi_0} = RTlna, \tag{43}$$

where ξ_0 is the activity when $(F - F_0)$ is equal to zero. $\frac{\xi}{\xi_0}$ is then the relative activity (a), and it is in this sense that the function is commonly employed.

Similarly, the relative activity of a molecular or ionic species in a phase of variable composition will be related to the partial free energy by the equation

$$\overline{F} - \overline{F}_0 = RTlna. \tag{44}$$

The relative activity will be called the activity in all subsequent discussions.

The Equilibrium Constant of a Chemical Reaction: Let us now consider a reaction at constant temperature and pressure in which n_1 mols of A_1, etc., n_2 mols of A_2, etc., and n_3 mols of A_3, etc., react to form n_1' mols of A_1', etc., n_2'

[1] Lewis and Randall, *J. Am. Chem. Soc.*, **43**, 1112 (1921); Thermodynamics, Chaps. XXII to XXVII inclusive.

[2] *J. Am. Chem. Soc.*, **42**, 761 (1920).

[3] *Z. physik. Chem.*, **104**, 406 (1923).

[4] Lewis and Randall, Thermodynamics, Chaps. XVII–XX inclusive.

mols of A_2', etc., and n_3' mols of A_3', etc., where the mols with the subscript 1 refer to gases, 2 to solutions, and 3 to liquids and solids. Thus

$$n_1A_1 + \cdots n_2A_2 + \cdots n_3A_3 + \cdots = n_1'A_1' + \cdots n_2'A_2' + \cdots n_3'A_3'.$$

According to equations (43) and (44),

$$(F - F_0)_{A_1} = n_1RTlna_{A_1}, \text{ etc.},$$
$$(\overline{F} - \overline{F}_0)_{A_2} = n_2RTlna_{A_2}, \text{ etc.},$$

and

$$(F - F_0)_{A_1'} = n_1'RTlna_{A_1'}, \text{ etc.},$$
$$(\overline{F} - \overline{F}_0)_{A_2'} = n_2'RTlna_{A_2'}, \text{ etc.}$$

The total change in free energy of the reaction will be

$$[(F - F_0)_{A_1'} + (\overline{F} - \overline{F}_0)_{A_2'} + \cdots] - [(F - F_0)_{A_1} + (\overline{F} - \overline{F}_0)_{A_2} + \cdots]$$
$$= RTln \frac{a_{A_1'}^{n_1'} \cdots a_{A_2'}^{n_2'} \cdots a_{A_3'}^{n_3'} \cdots}{a_{A_1}^{n_1} \cdots a_{A_2}^{n_2} \cdots a_{A_3}^{n_3} \cdots}.$$

If we let

$$\Delta F = (F_{A_1'} + \overline{F}_{A_2'} + \cdots) - (F_{A_1} + \overline{F}_{A_2} + \cdots)$$

and

$$\Delta F_0 = (F_{0A_1'} + \overline{F}_{0A_2'} + \cdots) - (F_{0A_1} + \overline{F}_{0A_2} + \cdots),$$

we obtain

$$\Delta F - \Delta F_0 = RTln \frac{a_{A_1'}^{n_1'} \cdots a_{A_2'}^{n_2'} \cdots a_{A_3'}^{n_3'}}{a_{A_1}^{n_1} \cdots a_{A_2}^{n_2} \cdots a_{A_3}^{n_3}}. \qquad (45)$$

ΔF is the free energy change of the reaction in general, and $(\Delta F - \Delta F_0)$ is the free energy change of the reaction in reference to the standard state.

When the reaction is in equilibrium at constant temperature and pressure, the condition that

$$\Delta F = 0 \qquad (21)$$

must be fulfilled, and, consequently,

$$\Delta F_0 = -RTln \frac{a_{A_1'}^{n_1'} \cdots a_{A_2'}^{n_2'} \cdots a_{A_3'}^{n_3'} \cdots}{a_{A_1}^{n_1} \cdots a_{A_2}^{n_2} \cdots a_{A_3}^{n_3} \cdots}. \qquad (46)$$

Since ΔF_0 is a constant, we have at constant temperature and pressure

$$K = \frac{a_{A_1'}^{n_1'} \cdots a_{A_2'}^{n_2'} \cdots a_{A_3'}^{n_3'} \cdots}{a_{A_1}^{n_1} \cdots a_{A_2}^{n_2} \cdots a_{A_3}^{n_3} \cdots}, \qquad (47)$$

where K is the equilibrium constant of the reaction. This general equation, which is entirely similar in form to the mass action law, has the advantage of being exact.

The Activity Product, the Mean Activity Product, and the Activity Coefficient of an Electrolyte: The equilibrium constant of dissociation of a uni-

univalent electrolyte may now be written

$$K = \frac{a_+ a_-}{a_2}, \tag{48}$$

where a_+, a_- are the activities of the cation and anion, respectively, and a_2 is the activity of the undissociated molecule. According to equation (46),

$$\Delta F_0 = -RTln\frac{a_+'' a_-''}{a_2''} = RTlna_2'' - RTlna_+'' a_-''$$

and

$$\Delta F_0 = -RTln\frac{a_+' a_-'}{a_2'} = RTlna_2' - RTlna_+' a_-',$$

where the primes and double primes refer to solutions of two different concentrations, respectively. Since ΔF_0 is constant, by subtracting the second of these equations from the first, and letting $\overline{F}_1$ and $\overline{F}_2$ be the partial free energies at the two concentrations, respectively, we obtain according to equation (44)

$$\overline{F}_2 - \overline{F}_1 = RTln\frac{a_2''}{a_2'} = RTln\frac{a_+'' a_-''}{a_+' a_-'}. \tag{49}$$

In view of the fact that in solutions of strong electrolytes the concentration of the undissociated molecule if present at all is unknown, and since our chief concern is with partial molal free energy differences and activity ratios, we let the equilibrium constant equal unity, and define the activity of the electrolyte by

$$a_2 = a_+ a_-$$

and the mean activity of the electrolyte by

$$a_\pm = (a_+ a_-)^{1/2}.$$

Further, the activity coefficient of a uniunivalent electrolyte is defined as the mean activity product of its ions divided by the molal concentration of the electrolyte. The activity coefficient, γ, of a uniunivalent electrolyte will be accordingly

$$\gamma = \frac{a_\pm}{m} = \left(\frac{a_+ a_-}{m^2}\right)^{1/2} \tag{50}$$

or the square root of the product of the activity coefficients of the ions. In general, if we consider the dissociation of any strong electrolyte of a molal concentration m according to

$$C_{\nu^+}A_{\nu^-} = \nu^+ C^+ + \nu^- A^-,$$

we shall have

$$a_2 = a_+^{\nu^+} a_-^{\nu^-}$$

and

$$a_\pm = (a_+^{\nu^+} a_-^{\nu^-})^{1/\nu},$$

where ν, the total number of ions formed, will equal $\nu^+ + \nu^-$. The activity coefficient will be given by

$$\gamma = \left(\frac{a_+^{\nu^+} a_-^{\nu^-}}{(\nu^+ m)^{\nu^+} (\nu^- m)^{\nu^-}} \right)^{1/\nu} = \frac{a_\pm}{m(\nu^{+\nu^+} \nu^{-\nu^-})^{1/\nu}} \tag{51}$$

or the νth root of the product of the activity coefficients of the ions.

The Free Energy Increment of a Perfect Gas and Perfect Solute at Constant Temperature: According to equation (6), the free energy is

$$F = A + pv, \tag{6}$$

which upon differentiation becomes

$$dF = dA + pdv + vdp.$$

In any reversible isothermal expansion or compression of a gas, the decrease in A will equal the maximum work, or

$$dA = -pdv,$$

and, therefore,

$$\partial F = vdp.$$

Since, for a perfect gas, $pv = RT$, we obtain

$$\partial F = RT\partial lnp = RT\partial lnm. \tag{52}$$

For a finite change between two concentrations, it is evident that

$$F_2 - F_1 = RTln\frac{m_2}{m_1}. \tag{53}$$

If the process consists of an expansion, or $m_1 > m_2$, it will be accompanied by a decrease in free energy.

In an analogous manner, on the assumption of the validity of van't Hoff's law ($\pi = mRT$) for perfect solutes, it can be shown that

$$\partial \overline{F} = RT\partial lnm, \tag{54}$$

where $\overline{F}$ and m are the partial free energy and concentration of the solute.

Equations (52) and (54), which are exactly analogous to equation (40), approach exact validity as m approaches zero.

The Limiting Law for Dilute Molecular and Ionic Species: From the fundamental definition of the activities of gases, undissociated solutes and electrolytes, we obtain by differentiation at constant temperature the equations

$$\partial F = RT\partial lna, \tag{55}$$

$$\partial \overline{F} = RT\partial lna, \tag{56}$$

$$\partial \overline{F} = \nu RT\partial lna_\pm, \tag{57}$$

respectively. We may now state the limiting law for molecular and ionic species at high dilutions in the following simple manner: *The activities of all molecules and ions approach proportionality to their concentrations as their concentrations approach zero.* It is at once obvious that equations (55), (56) and (57) become equal to (52), (54) and (40) as the concentrations of the species under consideration approach zero. (40), (52) and (54) are, consequently, particular cases of a general law. From this law and the definition of the activity, the law for ideal gases, van't Hoff's law for undissociated molecules, and Raoult's law may be deduced.[1] As a result of this important property of the activity of ions and molecules, the general expression for the equilibrium constant of a reaction (equation 47) approaches in value the well-known mass action law

$$K = \frac{m_{A_1'}^{n_1'} \cdots m_{A_2'}^{n_2'} \cdots}{m_{A_1}^{n_1} \cdots m_{A_2}^{n_2} \cdots}, \tag{47a}$$

as the concentrations of the gas and solute components approach zero. The law of mass action is thus shown to be a limiting law, which will not be valid in gas systems at high pressures, and solutions of high concentrations.

Attempts to apply the law of mass action to solutions of strong electrolytes in aqueous solutions have always met with failure with the possible exception of some results obtained with very dilute solutions. This is due both to an inadequate knowledge of the true concentrations of the ions and molecules in the solution, and to the fact that the classic mass action law has been employed. The general law of mass action expressed by equation (47) should prove of great value in the future for calculating the inner equilibrium of solutions.

Activity and Temperature: We have found that the variation of the free energy with the temperature is given by

$$\frac{\partial\left(\frac{F}{T}\right)}{\partial T} = -\frac{H}{T^2}, \tag{17}$$

where F and H are to be referred to arbitrary standard states. Further, according to equation (29), the free energy of a phase of c components is expressed by

$$F = N_1\overline{F}_1 + N_2\overline{F}_2 + \cdots + N_c\overline{F}_c, \tag{29}$$

or, if each of these quantities be referred to arbitrary standard states,

$$F - F^0 = N_1(\overline{F}_1 - \overline{F}_1{}^0) + N_2(\overline{F}_2 - \overline{F}_2{}^0) + \cdots + N_c(\overline{F}_c - \overline{F}_c{}^0) \tag{58}$$

is obtained. We may now introduce the activities by equation (44) and obtain

$$F - F^0 = N_1RT\ln a_1 + N_2RT\ln a_2 + \cdots + N_cRT\ln a_c. \tag{59}$$

[1] The ideal gas laws are immediately deducible. From (55) and the limiting law, $v\partial p = RT\partial \ln m$, whence by integration $pv = RT$ since the integration constant is zero.

Similarly, according to the general equation for partial quantities and equation (36), the total heat content will be

$$H - H^0 = N_1\bar{L}_1 + N_2\bar{L}_2 + \cdots + N_c\bar{L}_c. \tag{60}$$

Substituting these values of $(F - F^0)$ and $(H - H^0)$ for F and H in equation (17), and performing the differentiation at constant composition, we obtain

$$\left[\frac{N_1\partial ln a_1 + N_2\partial ln a_2 + \cdots + N_c\partial ln a_c}{dT}\right]_{p,\,N} = \frac{-(N_1\bar{L}_1 + N_2\bar{L}_2 + \cdots N_c\bar{L}_c)}{RT^2}. \tag{61}$$

This is the general equation for the variation of the activities of the components of a mixture with the temperature and at constant composition.

Let us consider the case where "1 mol of solution," which consists of N_1 mols of the first component, N_2 mols of the second component, etc., is transferred from a solution of one composition to that of another composition. In this case, the partial free energy and heat content increments will be

$$F'' - F' = N_1(\bar{F}_1'' - \bar{F}_1') + N_2(\bar{F}_2'' - \bar{F}_2') + \cdots + N_c(\bar{F}_c'' - \bar{F}_c') \tag{58a}$$

$$= N_1RTln\frac{a_1''}{a_1'} + N_2RTln\frac{a_2''}{a_2'} + \cdots + N_cRTln\frac{a_c''}{a_c'} \tag{59a}$$

and

$$H'' - H' = N_1(\bar{L}_1'' - \bar{L}_1') + N_2(\bar{L}_2'' - \bar{L}_2') + \cdots + N_c(\bar{L}_c'' - \bar{L}_c'). \tag{60a}$$

Substituting these values for ΔF and ΔH in equation (18), and performing the differentiation at constant composition, we obtain

$$\left[\frac{N_1\partial ln\frac{a_1''}{a_1'} + N_2\partial ln\frac{a_2''}{a_2'} + \cdots + N_c\partial ln\frac{a_c''}{a_c'}}{\partial T}\right]_{p,\,N} = -\frac{[N_1(\bar{L}_1'' - \bar{L}_1') + N_2(\bar{L}_2'' - \bar{L}_2') + \cdots N_c(\bar{L}_c'' - \bar{L}_c')]}{RT^2}. \tag{61a}$$

Usually, the transfer of 1 mol of a single component is considered. In this case, it is obvious that

$$\frac{\partial\left(ln\frac{a''}{a'}\right)}{\partial T} = -\frac{(\bar{L}'' - \bar{L}')}{RT^2}. \tag{62}$$

Although many symbols are required to perform these deductions accurately, the principles involved are quite simple. If 1 mol of a component is transferred, then ΔF is the partial free energy change and ΔH is the relative partial heat content change of the transfer. If 1 mol of solution is transferred,

then ΔF is the mol fraction times the partial free energy change of the first component plus the mol fraction times the partial free energy change of the second component, etc., and ΔH is the mol fraction times the relative partial heat content change of the first component plus, etc.

In order to integrate equation (62), or others like it, it is necessary to know $(\overline{L}'' - \overline{L}')$ as a function of the temperature. Such a relation is given by equation (11), from which it is clear that

$$\frac{\partial(\overline{L}'' - \overline{L}')}{\partial T} = \overline{C}_p'' - \overline{C}_p', \tag{63}$$

where $\overline{C}_p''$ and $\overline{C}_p'$ are the partial molal specific heats at constant pressure at the two concentrations, respectively.

Activity and Pressure: We have already found for the differential of the free energy at constant composition

$$\partial F = -S\partial T + v\partial p, \tag{13}$$

whence by differentiation with respect to p, at constant temperature, we obtain

$$\left[\frac{\partial F}{\partial p}\right]_T = v. \tag{64}$$

According to the general equation for partial quantities, the total volume V will be given by

$$V = N_1\overline{V}_1 + N_2\overline{V}_2 + \cdots + N_c\overline{V}_c, \tag{65}$$

where $\overline{V}_1$, $\overline{V}_2$, etc., are the partial volumes. Substituting for F the value given by (59), and for V the value given by (65), we obtain

$$\left[\frac{N_1\partial lna_1 + N_2\partial lna_2 + \cdots + N_c\partial lna_c}{\partial p}\right]_{T,N} = \frac{N_1\overline{V}_1 + N_2\overline{V}_2 + \cdots + N_c\overline{V}_c}{RT} \tag{66}$$

and for a single component

$$\left[\frac{\partial lna}{\partial p}\right]_{T,N} = \frac{\overline{V}_1}{RT}. \tag{67}$$

The Condition of Equilibrium of a Polycomponent System in More than One Phase at Constant Pressure and Temperature: As previously mentioned, Gibbs proved the general case that when a c component system in P phases is in equilibrium at constant temperature and pressure, the values of the chemical potential, $\frac{\partial F}{\partial m}$, of each component will be the same in each phase (equation 25). That this is true for a particular case can be immediately seen by considering the distribution of a component between two liquid phases at constant temperature and pressure, and the process of transfer of the component from one phase to the other. Any change in free energy in such a process will equal the

difference in partial free energies of the component in the two phases, respectively. But the criterion of equilibrium at constant temperature and pressure is that $\partial F = 0$, and, consequently, the partial free energies of the component in the two phases must be equal. This is equivalent to the statement that at equilibrium the activities of the component in the two phases are equal. If the partial free energy of the component is greater in the first phase than in the second, we have found that it will tend to pass from the first phase to the second with an accompanying loss in free energy. Consequently, when the activity of a component distributed through two phases is greater in the first phase than in the second, the component may pass from the first phase to the second.

Summary: In this section, the important properties of the activity function have been discussed and the general equations have been deduced. The properties of this function have been shown to rest on the definition of the relative activity, which for a component of a one-component system is

$$F - F_0 = RT\ln a, \tag{43}$$

and for a component in a phase of more than one component is

$$\overline{F} - \overline{F}_0 = RT\ln a. \tag{44}$$

The limiting law for molecular or ionic species at high dilutions has been stated as follows: "The activities of all molecules and ions approach proportionality to their concentrations as their concentrations approach zero." From this law and the definitions of activities, the gas laws and the laws of dilute solutions may be readily deduced.

It has been found that if the activity of a substance distributed through two phases is greater in the first phase than in the second, it may pass spontaneously from the first phase to the second. The criterion of stable equilibrium is that the activities of all components distributed through all phases be equal.

By employing the activity function, a general law of equilibrium may be deduced, of which the law of mass action is a special case, valid in dilute systems, and exact in infinitely dilute systems.

The general equations which express the relations of the activities of a phase of more than one component to the variables, pressure, temperature and composition are:

(1) *Temperature and Pressure Constant:* From (30) and the definition of activity,

$$\left[\frac{N_1\partial\ln a_1 + N_2\partial\ln a_2 + \cdots + N_c\partial\ln a_c}{\partial N}\right]_{p,\,T} = 0. \tag{68}$$

(2) *Pressure and Composition Constant:*

$$\left[\frac{N_1\partial\ln a_1 + N_2\partial\ln a_2 + \cdots + N_c\partial\ln a_c}{\partial T}\right]_{p,N} = -\frac{[N_1\overline{L}_1 + N_2\overline{L}_2 + \cdots + N_c\overline{L}_c]}{RT^2}. \tag{61}$$

(3) *Temperature and Composition Constant:*

$$\left[\frac{N_1\partial\ln a_1 + N_2\partial\ln a_2 + \cdots + N_c\partial\ln a_c}{\partial p}\right]_{T,N} = \frac{N_1\overline{V}_1 + N_2\overline{V}_2 + \cdots + N_c\overline{V}_c}{RT}.^{1} \tag{66}$$

[1] Equations 68, 61 and 66 were originally deduced by Lewis, *Proc. Amer. Acad.*, 43, 259 (1907).

These considerations and equations will serve as a general basis for the thermodynamics of solutions, and may by simple transformations be adapted to a specific problem. In the following discussion, we shall apply this method to electromotive forces, freezing points, vapor pressures, solubilities, etc., of strong electrolytes, and compute by typical methods the values of the activities of these electrolytes.

Calculations of the Activity Coefficients of Strong Electrolytes

It is possible to determine the activity coefficient of an electrolyte by electromotive force measurements of cells without liquid junction, and from the measurements of any of the colligative properties of solutions. On closer examination, however, this is a task accompanied with considerable difficulty. The activity coefficient has been so defined that it must equal unity at zero concentration, and it is on this value that all other values must be based. As a consequence, it is necessary to extrapolate the experimental results to infinite dilution by graphical methods, or employ some empirical equation which expresses the colligative property as a function of the concentration, and then perform an integration between a finite and zero concentration. It is just such an extrapolation or calculation which is subject to considerable error, because of the difficulty in obtaining reliable or accurate measurements at very low concentrations.

Measurements of rise in boiling point involve too many experimental difficulties to furnish the desired degree of accuracy at low concentrations, and would give only the activity coefficients at the boiling point of the solution. The difficult measurement of the osmotic pressure would obviously not suffice.

In order to perform the graphical extrapolation without considerable error, it is necessary to have consistent and reliable data in the concentration range from 0.001 or less to 0.1 molal. According to the data of Lovelace, Frazer, and Sease,[1] a 0.0498 molal potassium chloride solution has a vapor pressure only 0.0293 mm. lower than the vapor pressure of water at 20°. Although vapor pressure measurements will be shown to be of great value at high concentrations, it is clear from the order of their magnitude that they would become increasingly less valuable as the concentration decreases.

The measurement of the lowering of the freezing point, which has been greatly improved in recent years by the newer methods of measuring temperature and temperature differences, is much more promising. But, in this case, the results of the measurement must be reliable to within 0.0001°, or even less, to warrant an accuracy of 1 per cent in the calculated activity coefficients.

Theoretically, the electromotive force method should be the most accurate for, according to equation (41), the electromotive force of a concentration cell is roughly proportional to the logarithm of the ratio of the concentrations of the solutions in the two parts of the cell. With the galvanometers at present available, there should be little difference in accuracy in measuring a cell containing, in the first place, solutions of 1 and 0.1 molal concentrations, and, in the second place, solutions of 0.001 and 0.0001 molal concentrations. Consequently, the measurement of a reversible cell should yield equally accurate results in dilute and in concentrated solutions. The electromotive forces of many cells have been found to be re-

[1] *J. Am. Chem. Soc.*, **43**, 102 (1921).

producible to within a few hundredths of a millivolt in very dilute solutions, but it is probable that, in most cases, these measurements are not of great value for computing activity coefficients by extrapolation because of slight electromotive forces produced by side reactions, or other obscure causes depending on the methods of preparation and nature of the surfaces of the solids involved. These disturbing factors, which are negligible in concentrated solutions, are a great drawback to the electromotive force method of computing activity coefficients in very dilute solutions. It is very difficult indeed to discover whether such complications exist; still more difficult to discover why they exist, and to eliminate them. There are, however, some few cell measurements which are thought to be sufficiently exact at all concentrations down to 0.001 molal to warrant an extrapolation to zero concentration.

As a result of this cursory review of the available methods, it is clear that only by considerable experimental exactitude, as well as laborious calculation, and by comparison of results by different methods can certainty regarding the values for the activity coefficients be assured.

Calculation by Extrapolation from Electromotive Force Data: We have seen that equation (49) is

$$\overline{F}_2 - \overline{F}_1 = RTln\frac{a_+''a_-''}{a_+'a_-'} = 2RTln\frac{a_\pm''}{a_\pm'} \tag{49}$$

and $\overline{F}_2 - \overline{F}_1$ equals $(-\mathbf{NEF})$ of a concentration cell without liquid junction containing a uniunivalent electrolyte if the cell reaction transfer is from left to right according to C^+A^- (dil.) = C^+A^- (conc.). Therefore, if we let $\mathbf{E}$ represent the electromotive force of such a cell, and $\mathbf{E}_0$ the electromotive force of a standard state such that $a_\pm^0$ equals unity, we obtain, at 25°,

$$-(\mathbf{E} - \mathbf{E}_0) = \frac{2RT}{\mathbf{NF}}lna_\pm = 0.1183 \log a_\pm. \tag{69}$$

By subtracting $0.1183 \log m$ from both members, and remembering that γ equals $\frac{a_\pm}{m}$, we obtain

$$\mathbf{E}_0 - (\mathbf{E} + 0.1183 \log m) = 0.1183 \log \gamma. \tag{70}$$

Since γ equals unity when m equals zero, the right-hand member of this equation vanishes, and $\mathbf{E}_0$ equals $(\mathbf{E} + 0.1183 \log m)$ at zero concentration. If sufficiently reliable results are available in dilute solutions, $\mathbf{E}_0$ may be evaluated graphically by extrapolating the plot of $(\mathbf{E} + 0.1183 \log m)$ against m, or, for the convenience of plotting, $m^{1/2}$. It is impossible to extrapolate directly partial molal free energy data, and, consequently, electromotive force data to infinite dilution, since the partial free energy of an electrolyte equals $-\infty$ when m equals zero. By employing the activity coefficient, the extrapolation is made possible. This is one of the most important uses of the activity function.

Up to the present time, there appear to be available electromotive force measurements of only a few cells which are sufficiently accurate and reliable in very dilute solutions to permit the extrapolation by means of equation (70) with any degree of certainty. Of these, we cite the measurements of a number

of investigators [1] on the cell:

$$H_2 | HCl(m) | AgCl | Ag.$$

There seems to be some doubt as to the value of E_0 obtained by this method of extrapolation. From Linhart's data, Lewis and Randall obtained 0.2234 volt for E_0. Scatchard later obtained 0.2226 volt by employing the same data, Nonhebel obtained 0.2228 volt from his own measurements combined with those of Linhart, and more recently Randall and Young have obtained 0.2221 volt. That such a difference is obtained in the values of E_0 extrapolated by different investigators is good evidence of the difficulty of obtaining measurements of sufficient accuracy in the dilute solutions so that all doubt as to the numerical value of the standard potential is eliminated.

Although the electromotive force measurements are not usually sufficiently accurate in dilute solutions to be extrapolated by this direct method, they have proved to be of great value for the calculation of activity coefficients in the more concentrated solutions. In the first place, if we know the activity coefficient at a given concentration, then by equation (49) it may be computed at another concentration. In the second place, an extrapolation of the electromotive force measurements at high concentrations may be made by the use of method and equation of Hückel.[2] In view of these difficulties, data from other sources have been employed for the determination of activity coefficients. Of these, the determination of the lowering of the freezing point has proved to be of considerable value.

Activity Coefficients from Freezing Point Lowerings in Very Dilute Solutions: The first calculations of activity coefficients from freezing point data were made by Lewis.[3] Later the method has been developed in very dilute solutions by Lewis and Linhart,[4] and extended to concentrated solutions by Lewis and Randall.[5] The complicated calculation of the activity coefficient from freezing point lowerings at temperatures other than the freezing point of the solution and at moderately high concentrations has been made by Lewis and Randall in the cases of sodium chloride and sulphuric acid solutions. In the present discussion, a presentation of the calculation of Lewis and Linhart will be made, and the factors which must be included in order to extend the calculation to high concentrations will be indicated.

Consider the reaction

$$H_2O\ (l) = H_2O\ (s) + (-\Delta H).$$

$(-\Delta H)$ will equal the heat of fusion, or ΔH the heat of solidification. Let T_0

[1] Linhart, *J. Am. Chem. Soc.*, **39**, 2601 (1917); **41**, 1175 (1919); Scatchard, *J. Am. Chem. Soc.*, **47**, 641 (1925); Nonhebel, *Phil. Mag.*, (7) **2**, 1085 (1926); Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); Randall and Young, *J. Am. Chem. Soc.*, **50**, 989 (1928).

[2] Hückel, *Physik. Z.*, **26**, 93 (1925). This powerful method of extrapolation will be discussed in a later section.

[3] *J. Am. Chem. Soc.*, **34**, 1631 (1912).

[4] *J. Am. Chem. Soc.*, **41**, 1951 (1919).

[5] *J. Am. Chem. Soc.*, **43**, 1112 (1921).

equal the temperature of the freezing point of pure water, T the temperature of the freezing point of the solution, and θ the lowering of the freezing point, and, therefore,

$$T = T_0 - \theta \qquad \text{and} \qquad dT = -d\theta.$$

In this case, the transfer is from the liquid to the solid. If, now, we let a' equal the activity of the liquid, and a'' the activity of the solid, we obtain the equation, similar to equation (62),

$$\frac{\partial ln \frac{a''}{a'}}{\partial T} = -\frac{\Delta H}{RT^2}. \tag{71}$$

If we choose as a reference state the condition that the activity of liquid water is unity at 0°, it is true that

$$\frac{\partial ln a''}{\partial T} = -\frac{\Delta H}{RT^2}. \tag{71a}$$

It is also true that at the freezing point of the solution, since the system is in equilibrium, the activity of the solid equals the activity of the liquid in the solution, or a'' equals a'.

According to equation (68), the activity of the solvent is related to the activity, a_2, of the solute as follows:

$$\partial ln a' = -\frac{N_2}{N_1}\partial ln a_2, \tag{68}$$

and, by substitution in (71a),

$$\partial ln a_2 = \frac{N_1}{N_2}\frac{\Delta H}{RT^2}\partial T.$$

Eliminating T, and the mol fractions, we obtain

$$\partial ln a_2 = \frac{55.5}{m}\frac{(-\Delta H)}{R(T_0 - \theta)^2}\partial\theta.$$

Since θ is small compared with T_0, it may be neglected and hence

$$\partial ln a_2 = \frac{55.5(-\Delta H)}{mRT_0^2}\partial\theta. \tag{72}$$

If it be assumed that $(-\Delta H)$ is constant over a range of temperature and equal to 1438 cals., its value at 0°, an error is introduced which invalidates the results at the higher concentrations. In the second place, a_2 is the activity of the solute at the freezing point. If the activity is desired at another temperature (e.g., 25°), a calculation according to equation (62) must be made. These two factors which are negligible in very dilute solutions (up to 0.01 molal), but important in concentrated solutions, involve for their calculation a knowl-

edge of the specific heats of water, ice, the partial heat content of the solute and its variation with the temperature, and the partial heat capacity of the solute.[1] In dilute solutions, these complications may be neglected, and, consequently, it is found that $\frac{RT_0^2}{55.5(-\Delta H)}$ equals 1.858°, or the molecular lowering of the freezing point for water. If we denote this fraction λ, equation (72) becomes

$$\partial ln a_2 = \frac{\partial \theta}{\lambda m} \cdot \tag{73}$$

This equation is valid within the experimental error for solutions of electrolytes of concentrations not exceeding 0.05 molal. Since a_2 is equal to $a_+^{\nu_+} a_-^{\nu_-}$ for any electrolyte,

$$\partial ln a_2 = \partial ln a_+^{\nu_+} a_-^{\nu_-} = \nu \partial ln a_\pm = \frac{\partial \theta}{\lambda m} \cdot \tag{74}$$

Dividing by ν, we obtain

$$\partial ln a_\pm = \frac{\partial \theta}{\nu \lambda m} \cdot \tag{75}$$

Lewis and Linhart found that the empirical function

$$\left[\nu\lambda - \frac{\theta}{m} \right] = \beta' m^{\alpha'} \tag{76}$$

is valid in dilute solutions of all electrolytes. β' and α' are empirical constants. If we take the logarithm of both members of this equation, we obtain

$$\log \left[\nu\lambda - \frac{\theta}{m} \right] = \log \beta' + \alpha' \log m. \tag{77}$$

It is then clear that by plotting $\log \left(\nu\lambda - \frac{\theta}{m} \right)$ against $\log m$, straight lines will be obtained from which β' and α' may be evaluated.

By transposing (76), differentiating and dividing by $\nu\lambda m$,

$$\frac{\partial \theta}{\nu \lambda m} = \partial ln m - \frac{\beta'(\alpha' + 1) m^{\alpha' - 1}}{\nu\lambda} \partial m \tag{78}$$

is obtained. This may be combined with (75) and the definite integral

$$\int_{a_0}^{a} \partial ln a_\pm = \int_{m_0}^{m} \partial ln m - \frac{\beta'(\alpha' + 1) m^{\alpha' - 1}}{\nu\lambda} \partial m$$

formed. When $m_0 = 0$, $a_{\pm_0} = m_0$, whence, upon substitution of $m\gamma$ for $a_\pm$,

[1] Lewis and Randall, *J. Am. Chem. Soc.*, **43**, 1112 (1921); Thermodynamics, Chaps. XXIII and XXVII; Randall and Bisson, *J. Am. Chem. Soc.*, **42**, 347 (1920).

integration, and conversion to common logarithms,

$$\log \gamma = -\frac{\beta'(\alpha' + 1)}{2.303\nu\lambda\alpha'} m^{\alpha'} \tag{79}$$

is obtained. Since β', α', ν and λ are constants in case of a given electrolyte in aqueous solution, it is seen that this equation may be written

$$\log \gamma = -\beta m^{\alpha'}, \tag{80}$$

where

$$\beta = \frac{\beta'(\alpha' + 1)}{2.303\nu\lambda\alpha'}. \tag{81}$$

In Fig. 5 is given a characteristic plot [1] of $\log\left(\nu\lambda - \frac{\theta}{m}\right)$ against $\log m$ of the

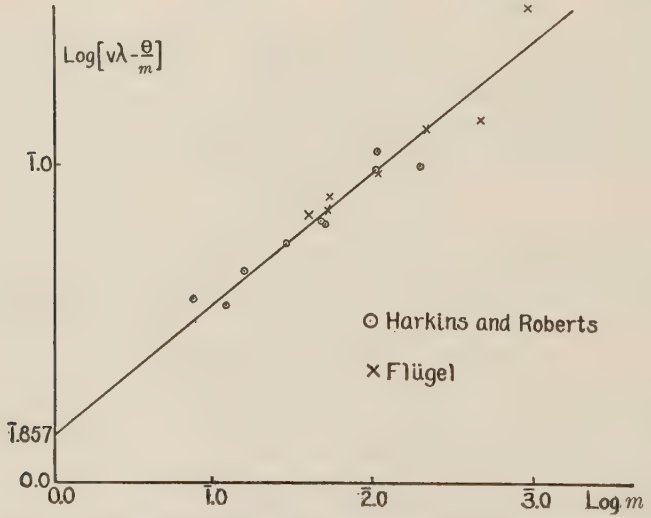

FIG. 5. Freezing Point Data of Dilute Sodium Chloride Solutions

combined freezing point data of Flügel,[2] and Harkins and Roberts [3] of dilute sodium chloride solutions. From the straight line drawn through the points, it is found that β' equals 0.720, α' equals 0.413, and, according to equation (81), β equals 0.288.

In Table VIII are given the activity coefficients of many electrolytes in dilute solutions obtained for the most part by this method, or by modifications

[1] Harned, *J. Am. Chem. Soc.*, **44**, 252 (1922).
[2] *Z. physik. Chem.*, **79**, 585 (1912).
[3] *J. Am. Chem. Soc.*, **38**, 2676 (1916).

TABLE VIII

ACTIVITY COEFFICIENTS IN VERY DILUTE SOLUTIONS FROM FREEZING POINT DATA

Electrolyte	Ref.	0.0001	0.0005	0.001	0.005	0.01	0.05	0.1
KCl	1; 8; 10; 11	——	——	0.961	0.926	0.903	0.817	0.767
KCl	2; 8; 10; 11	——	——	0.965	0.926	0.899	0.809	0.762
NaCl	1; 8; 9	——	——	0.963	0.928	0.906	0.825	0.772
NaCl	2; 8; 9	——	——	0.965	0.928	0.903	0.821	0.778
LiCl	2	——	——	0.965	0.927	0.901	0.819	0.779
HCl	6	——	——	0.965	0.928	0.904	0.829	0.796
TlCl	3	0.990	0.979	0.970	0.935	0.910	——	——
KNO_3	5; 11	0.994	0.984	0.976	0.943	0.916	0.806	0.732
HNO_3	7	——	——	——	0.930	0.905	0.827	0.784
KIO_3, NaIO	5; 13	0.99	0.97	0.96	0.915	0.882	0.765	0.692
K_2SO_4	5; 13	0.935	0.885	0.85	0.75	0.69	0.505	0.421
Na_2SO_4	4	——	0.920	0.89	0.78	0.719	0.537	0.449
H_2SO_4	4	——	0.912	0.876	0.734	0.648	0.424	0.341
$CoCl_2$	5; 13	0.94	0.90	0.87	0.78	0.73	——	——
$BaCl_2$	5; 13	0.94	0.89	0.865	0.77	0.72	0.568	0.501
$Ba(NO_3)_2$	4	——	0.915	0.884	0.770	0.701	0.501	0.408
$Pb(NO_3)_2$	3	0.964	0.921	0.890	0.770	0.692	0.463	0.367
$MgSO_4$	5; 12; 13	0.85	0.75	0.69	0.50	0.40	0.225	0.166
$CdSO_4$	5; 12	0.85	0.75	0.69	0.50	0.40	0.220	0.160
$CuSO_4$	5; 12; 14	0.85	0.75	0.69	0.50	0.40	0.216	0.158
$K_3Fe(CN)_6$	5; 14	0.92	0.85	0.81	0.66	0.57	——	——
$La(NO_3)_3$	5; 13	0.92	0.85	0.81	0.66	0.57	0.391	0.326

1. Harned, *J. Am. Chem. Soc.*, **44**, 252 (1922).
2. Scatchard, *J. Am. Chem. Soc.*, **47**, 648 (1925).
3. Randall and Vanselow, *J. Am. Chem. Soc.*, **46**, 2418 (1924).
4. Randall and Scott, *J. Am. Chem. Soc.*, **49**, 647 (1927).
5. Lewis and Linhart, *J. Am. Chem. Soc.*, **41**, 1951 (1919).
6. Randall and Young, *J. Am. Chem. Soc.*, **50**, 989 (1928).
7. Abel, Redlich and Lengyel, *Z. physik. Chem.*, **132**, 189 (1928).
8. Flügel, *Z. physik. Chem.*, **79**, 585 (1912).
9. Harkins and Roberts, **38**, 2676 (1916).
10. Jahn, *Z. physik. Chem.*, **79**, 585 (1912).
11. Adams, *J. Am. Chem. Soc.*, **37**, 494 (1915).
12. Hausrath, *Ann. Physik.* (4), **9**, 522 (1902).
13. Hall and Harkins, *J. Am. Chem. Soc.*, **38**, 2658 (1916).
14. Bedford, *Proc. Roy. Soc., London*, **83A**, 454 (1909).

of this method.[1] The values of the activity coefficients of sodium and potassium chlorides were obtained by Harned by equation (80) from the values of the constants β and α' given above. The other values for these electrolytes are the final values given by Schatchard, obtained from both freezing point and electromotive force measurements. The activity coefficients from 0.0001 to 0.01 for all electrolytes, obtained by Lewis and Linhart (Ref. 4) were computed by equation (79). The activity coefficients of these electrolytes at 0.05

[1] Scatchard, *J. Am. Chem. Soc.*, **47**, 648 (1925). Randall and Vanselow, ibid., **46**, 2418 (1924).

and 0.1 molal were computed by the equation which includes the correction caused by the variation of the latent heat of fusion of ice with the temperature. These values may be used at 0° or at 25°, since the temperature variation of activity coefficients of electrolytes in solutions of these dilutions is very small.

Activity Coefficients at High Concentrations from Electromotive Force Data: Cells of the type

$$\mathrm{Ag}\,|\,\mathrm{AgX}\,|\,\mathrm{MX}_n(m_1)\,|\,\mathrm{M}_x\mathrm{Hg}\,|\,\mathrm{MX}_n(m_2)\,|\,\mathrm{AgX}\,|\,\mathrm{Ag},$$

where $\mathrm{M}_x\mathrm{Hg}$ is an alkali or an alkali earth metal amalgam, and MX_n is an alkaline or alkaline earth halide, have been carefully studied. The relative partial free energies of the alkali sulphates have been obtained from measurements of the cells,

$$\mathrm{Hg}\,|\,\mathrm{Hg_2SO_4}\,|\,\mathrm{M_2SO_4}(m_1)\,|\,\mathrm{M}_x\mathrm{Hg}\,|\,\mathrm{M_2SO_4}(m_2)\,|\,\mathrm{Hg_2SO_4}\,|\,\mathrm{Hg},$$

and those of the hydroxides by means of the cells,

$$\mathrm{H_2}\,|\,\mathrm{MOH}(m_1)\,|\,\mathrm{M}_x\mathrm{Hg}\,|\,\mathrm{MOH}(m_2)\,|\,\mathrm{H_2}.$$

Although measurements of some of these cells were made at concentrations as low as 0.001 molal, the results cannot be used to extrapolate to zero concentration by equation (70), nor, at these low concentrations, are the activity coefficients determined from these results consistent with the freezing point data. This lack of concordance has been attributed to unavoidable side reactions.[1] At concentrations above 0.03 molal in the case of the uniunivalent halides, the agreement with the freezing point and other data is very good. The results at higher concentrations are therefore reliable and can be used for the calculation of the activity coefficients.

In the case of a uniunivalent halide, the electromotive force of the first of the above cells corresponds to the reaction,

$$C^+A^-(m_1) = \mathrm{C^+A^-}(m_2),$$

and therefore according to equation (49) we have

$$\Delta F = \overline{F}_2 - \overline{F}_1 = -\,\mathbf{NEF} = RT\ln\frac{a_+''a_-''}{a_+'a_-'}. \qquad (49)$$

A transfer from a dilute to a concentrated solution would be accompanied by an increase in free energy, and, therefore, **E** is positive when m_1 is greater than m_2. Since $a_\pm$ is equal to $(a_+a_-)^{1/2}$ and also to $m\gamma$, we obtain

$$-\,\mathbf{NEF} = 2RT\ln\frac{m''\gamma''}{m'\gamma'} \qquad (82)$$

or

$$\mathbf{E} = 0.1183\log\frac{m'\gamma'}{m''\gamma''} \qquad (82)$$

[1] Lewis and Randall, *J. Am. Chem. Soc.*, **43**, 1112 (1921).

at 25°. If then γ is known at one concentration, its value may be computed at another concentration.

In the case of the transfer of a biunivalent electrolyte,

$$-\mathbf{NEF} = RTln\frac{a_+''a_-''^2}{a_+'a_-'^2} \tag{49a}$$

is the equation for a cell of the first of the above types, **N** equals 2, $a_\pm$ equals $(a_+a_-^2)^{1/3}$ or, according to equation (51), $\gamma m(4)^{1/3}$ and, therefore

$$\mathbf{E} = 0.08873 \log\frac{m'\gamma'}{m''\gamma''}. \tag{83}$$

This is also the equation for the cells of the second of the above types containing sulphates.

The conditions are somewhat different with the cells containing the hydroxides since the transfer corresponding to the cell involves both that of the hydroxide and a water molecule.[1] Thus, the cell reaction is represented by

$$C^+A^-(m_1) + H_2O(m_2) = C^+A^-(m_2) + H_2O(m_1),$$

and the equation for the electromotive force becomes

$$\mathbf{E} = 0.1183 \log\frac{m'\gamma'}{m''\gamma''} + 0.1183 \log\frac{a_{H_2O(m'')}}{a_{H_2O(m')}}. \tag{84}$$

The second member on the right is not very large and may be readily evaluated.[2]

Table IX contains the values of the activity coefficients of a number of simple salts and the alkaline hydroxides determined by measurements of the above cells. We also include similar values for hydrochloric acid, and hydrobromic acid computed from measurements of the cells:

$$H_2|\,HX(m)\,|\,AgX\,|\,Ag.$$

The bracketed values were taken as the reference values. The values of the uniunivalent chlorides from 0.001 to 0.1 molal were taken from Table VIII. Suitable values for the iodides at 0.1 M were chosen. The reference values for the hydroxides, bromides, and bivalent salts were obtained by extrapolation by means of Hückel's equation.[3]

It is clear from this table that at constant temperature the activity coefficients first decrease, then pass through minimum values, and finally increase with increasing concentrations. These activity coefficients are plotted against the square root of ionic strength in Figs. 6, 7, and 8. The ionic strength, μ,

[1] Harned, *J. Am. Chem. Soc.*, **47**, 676 (1925).

[2] Harned, loc. cit.; Scatchard, *J. Am. Chem. Soc.*, **47**, 648 (1925); Harned and Swindells, ibid., **48**, 126 (1926).

[3] Hückel, *Physik. Z.*, **26**, 93 (1925); Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

TABLE IX

THE ACTIVITY COEFFICIENTS OF ELECTROLYTES AT HIGH CONCENTRATIONS CALCULATED FROM ELECTROMOTIVE FORCE DATA AT 25°

Electrolyte	Ref.	0.001	0.005	0.01	0.05	0.1	0.2	0.5	1.	1.5	2	2.5	3	3.5	4
KCl	1; 2; 14	0.965	0.926	0.899	0.815	(0.764)	0.712	0.644	0.597	0.576	0.569	0.568	0.571	0.571	0.581
NaCl	1; 2; 15	0.966	0.928	0.903	0.821	(0.778)	0.732	0.678	0.656	0.659	0.670	0.690	0.714	0.749	0.779
LiCl	1; 2; 3	0.965	0.927	0.901	0.819	(0.779)	0.756	0.725	0.757	0.819	0.919	1.040	1.174	1.358	1.554
HCl	4	0.965	0.928	0.904	0.829	(0.796)	0.766	0.757	0.810	0.903	1.019	1.151	1.320	1.520	1.762
KBr	2; 5; 16	——	——	——	0.8156	(0.765)	0.715	0.653	0.612	0.595	0.589	0.589	0.590	0.599	0.609
NaBr	2; 5	——	——	——	——	(0.779)	0.737	0.696	0.687	0.696	0.732	0.773	0.823	0.871	0.933
LiBr	2	——	——	——	——	(0.794)	0.769	0.758	0.806	0.890	0.999	1.152	1.293	1.519	1.829
HBr	6	——	——	0.906	0.831	0.802	0.779	0.788	0.873	——	1.169	——	1.671	——	——
KI	5	——	——	——	0.820	(0.775)	0.730	0.678	0.649	0.646	0.646	——	——	——	——
NaI	5	——	——	——	——	(0.788)	0.754	0.721	0.734	——	——	——	——	——	——
KOH	1; 7; 8	0.965	0.927	(0.901)	0.815	0.772	0.739	0.723	0.743	0.811	0.888	0.966	1.041	——	——
NaOH	9	——	0.925	(0.901)	0.809	0.765	0.723	0.679	0.667	0.690	0.728	0.770	0.812	0.855	——
LiOH	10	——	——	(0.899)	0.794	0.742	0.685	0.602	0.541	0.516	0.501	0.489	0.482	0.476	0.470
$BaCl_2$	11; 12; 18	——	——	(0.723)	0.554	0.495	0.439	0.395	0.398	——	——	——	——	——	——
$SrCl_2$	11; 12; 8	——	——	(0.729)	0.571	0.512	0.465	0.427	0.449	0.526	0.638	0.772	1.083	——	——
$CaCl_2$	11; 12; 8	——	——	(0.732)	0.582	0.528	0.492	0.510	0.725	1.065	1.555	——	3.385	——	——
K_2SO_4	13; 8	——	——	(0.720)	0.504	0.420	0.326	0.233	——	——	——	——	——	——	——
Na_2SO_4	13; 8	——	——	(0.721)	0.514	0.435	0.356	0.267	0.206	0.172	0.152	——	——	——	——
Li_2SO_4	13; 8	——	——	(0.722)	0.522	0.447	0.380	0.306	0.267	0.254	0.250	——	——	——	——

1. Scatchard, *J. Am. Chem. Soc.*, **47**, 648 (1925).
2. Harned, *J. Am. Chem. Soc.*, **51**, 416 (1929).
3. MacInnes and Beattie, *J. Am. Chem. Soc.*, **42**, 1117 (1920).
4. Randall and Young, *J. Am. Chem. Soc.*, **50**, 989 (1928).
5. Harned and Douglas, *J. Am. Chem. Soc.*, **48**, 3095 (1926).
6. James—Recent Measurements.
7. Knobel, *J. Am. Chem. Soc.*, **45**, 70 (1923).
8. Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).
9. Harned, *J. Am. Chem. Soc.*, **47**, 676 (1925).
10. Harned and Swindells, *J. Am. Chem. Soc.*, **48**, 126 (1926).
11. Lucasse, *J. Am. Chem. Soc.*, **47**, 743 (1925).
12. Harned, *J. Am. Chem. Soc.*, **48**, 326 (1926).
13. Åkerlöf, *J. Am. Chem. Soc.*, **48**, 1160 (1926).
14. MacInnes and Parker, *J. Am. Chem. Soc.*, **37**, 1445 (1915).
15. Pearce and Hart, *J. Am. Chem. Soc.*, **43**, 2483 (1921).
16. Allmand and Polack, *J. Chem. Soc.*, **115**, 1020 (1919).

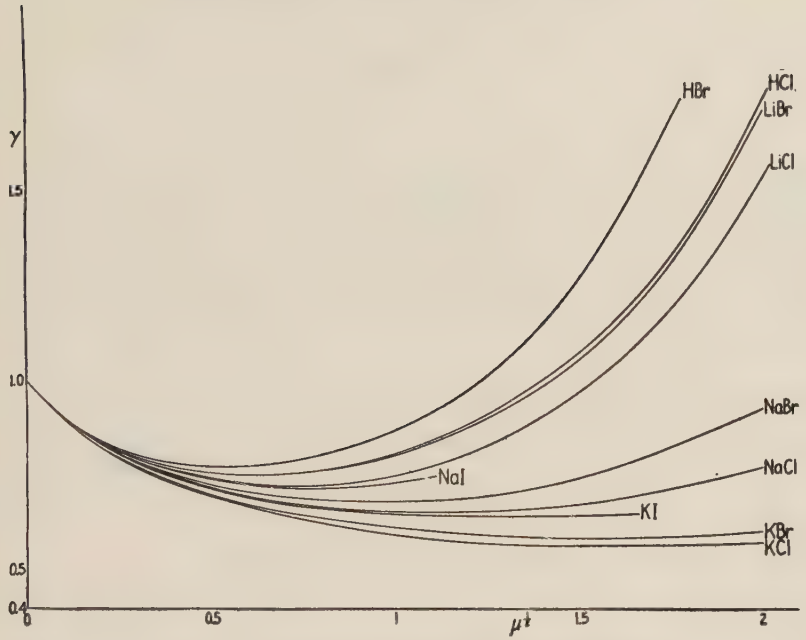

FIG. 6. Activity Coefficients of Uniunivalent Halides

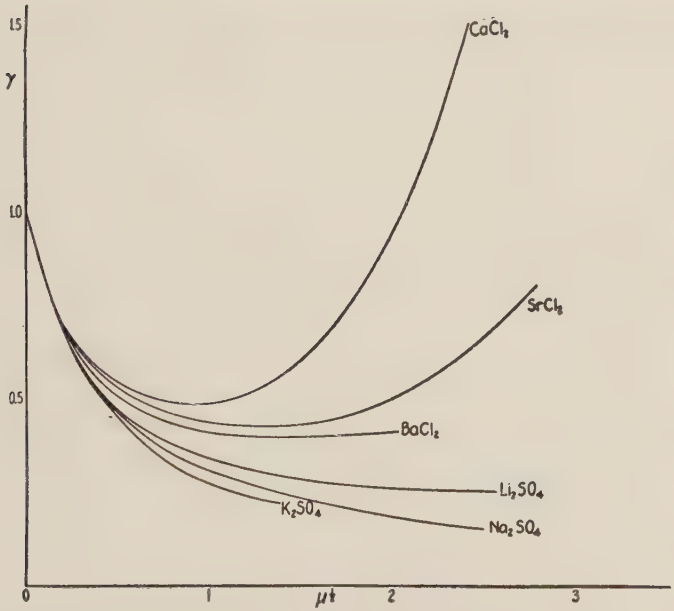

FIG. 7. Activity Coefficients of Alkaline Earth Chlorides and Alkali Sulphates

which was first employed by Lewis and Randall,[1] we define by the equation

$$\mu = \frac{\sum_{1}^{s} m_i z_i^2}{2}, \tag{85}$$

where m_i and z_i are the molal concentrations and valence of an ion of the ith kind respectively, and where the summation is for all the ions, $1 \cdots i \cdots s$, in the solution. This way of expressing the concentration we shall use continually and its importance will become apparent as we develop the theory of these solutions. We may summarize the results as follows:

(1) The activity coefficients of the uniunivalent halides at a given strength are in the order

$$\gamma_{HBr} > \gamma_{HCl} > \gamma_{LiBr} > \gamma_{LiCl} > \gamma_{NaI} > \gamma_{NaBr} > \gamma_{NaCl} > \gamma_{KI} > \gamma_{KBr} > \gamma_{KCl}. \tag{86}$$

(2) The order of the activity coefficients of the hydroxides is:

$$\gamma_{KOH} > \gamma_{NaOH} > \gamma_{LiOH}, \tag{87}$$

which is the reverse of that of the corresponding halides.

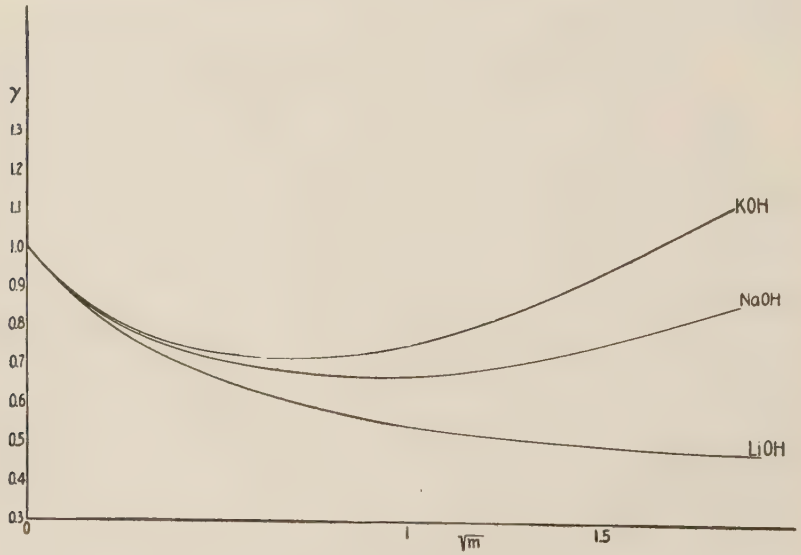

FIG. 8. Activity Coefficients of Alkali Hydroxides

(3) The order of the alkali sulphates is the same as that of the corresponding chlorides, namely:

$$\gamma_{Li_2SO_4} > \gamma_{Na_2SO_4} > \gamma_{K_2SO_4}. \tag{88}$$

[1] Lewis and Randall, *J. Am. Chem. Soc.*, **43**, 1112 (1921).

Further, at a given ionic strength,

$$\gamma_{CaCl_2} > \gamma_{SrCl_2} > \gamma_{BaCl_2}. \tag{89}$$

THE ACTIVITY COEFFICIENT AND OTHER COLLIGATIVE PROPERTIES. GENERAL CONSIDERATIONS RELATING TO SOLUTION THEORY

The Activity of a Volatile Component and its Vapor Pressure: When a volatile component of a solution is in equilibrium with its vapor, the activity of the component in the solution, a_1, is equal to its activity in the vapor state, a_v, and, according to equation (56),

$$\partial \overline{F}_1 = RT\partial ln a_1 = RT\partial ln a_v. \tag{56}$$

From the law of dilute systems, and the definition of activity, it immediately follows that the gas laws hold for the dilute vapor, and that a_v is proportional to the concentration and also to the pressure of the vapor, p_1, in dilute gases. In general, then, for a volatile component, at pressure ranges where the gas laws are valid for the vapor,

$$\partial \overline{F}_1 = RT\partial ln p_1, \tag{90}$$

and, in case of a second volatile component,

$$\partial \overline{F}_2 = RT\partial ln p_2. \tag{90}$$

It has previously been shown that the activities of two components in a solution at constant pressure and temperature are related by

$$N_1\partial ln a_1 + N_2\partial ln a_2 = 0. \tag{68}$$

If both are volatile,

$$N_1\partial ln p_1 + N_2\partial ln p_2 = 0$$

is obtained, an equation originally derived independently by Gibbs and by Duhem [1] which is valid for the range of vapor pressures over which the law of the ideal gas holds. Equation (68) permits the calculation of the activity of the volatile component from its vapor pressure, and also the activity of the volatile component from the activity of the non-volatile component.

Let us now consider the transfer of a mol of the volatile component from the solution to pure solvent, and let $\overline{F}_0$, a_0, p_0 refer to the partial free energy, activity and vapor pressure of the solvent, respectively. This change will be accompanied by a decrease in free energy, and consequently, according to (56) and (90),

$$(-\Delta\overline{F}) = -(\overline{F}_1 - \overline{F}_0) = RTln\frac{a_0}{a_1} = RTln\frac{p_0}{p_1}. \tag{91}$$

[1] *Compt. rend.*, **102**, 1449 (1886).

Let the activity of the pure component equal unity, whence $\overline{F}_0$ will equal zero, a_1 will be the relative activity, and

$$\overline{F}_1 = RTlna_1 = RT\int_{p_0}^{p_1} \partial lnp = RTln\frac{p_1}{p_0}. \tag{92}$$

Employing these conventions, the relative activity is equal to the ratio of the vapor pressure of the component in the solution to the vapor pressure of the pure component.

Calculation of the Activity Coefficient of the Solute from its Partial Vapor Pressure: In general, the activity of a component in a solution is equal to its activity in the vapor phase if the system solution-vapor is in equilibrium. If the component in question is an electrolyte, then according to (51)

$$\gamma \propto \frac{(a_2)^{1/\nu}}{m}.$$

If the partial vapor pressure, p_2, of this component is small, then it will be proportional to a_2 and

$$\gamma k = \frac{(p_2)^{1/2}}{m}. \tag{93}$$

A verification of this principle may be obtained from the results of Bates and Kirschmann[1] who measured the partial vapor pressure of hydrogen chloride above aqueous solutions of concentrated hydrochloric acid. In this case γ is proportional to $p^{1/2}/m$. If γ be assigned the same value at 4 molal as determined by the electromotive force method, the proportionality factor may be determined, and γ may then be calculated from the vapor pressures at the other concentrations. Such a calculation has been made and the results are given in Table X.

TABLE X

Comparison of the Activity Coefficient of Hydrochloric Acid from Electromotive Force and Vapor Pressure Data

$k = 0.000695$ (p(atms))

m	p (mm.)	γ (E.M.F.)	γ (V.P.)
4	0.0182	(1.76)	(1.76)
5	0.0530	2.40	2.40
6	0.140	3.25	3.25
7	0.348	4.46	4.40
8	0.844	6.03	5.99
9	1.93	7.96	8.06
10	4.20	10.18	10.69

Calculation of the Activity Coefficient of the Solute from Its Partition Coefficient: Exactly similar considerations as those relating to the vapor

[1] Bates and Kirschmann, *J. Am. Chem. Soc.*, **41**, 1991 (1919).

pressure are applicable in the case of the distribution of an electrolyte between two liquid phases, provided that it is undissociated in one of the phases and also that its concentration is not high in that phase. If these conditions are fulfilled, a_1 will be proportional to m', the concentration in the phase in which the electrolyte is undissociated, and, therefore

$$\gamma k = \frac{(m')^{1/\nu}}{m}, \tag{94}$$

where m is the concentration of the electrolyte in the phase in which it is dissociated. Randall and Failey [1] have recently applied this principle for the determination of the activity coefficients of some weak organic acids.

Calculation of the Activity Coefficient of the Solute from the Partial Vapor Pressure of Solvent: By rearranging equation (68), and letting a_1 equal the activity of the solvent and a_2 the activity of the solute, the equation

$$\partial ln a_2 = -\frac{N_1}{N_2}\partial ln a_1 \tag{68a}$$

is obtained. a_1, the relative activity referred to pure solvent, has been shown to equal $\frac{p_1}{p_0}$, where p_1 is the vapor pressure of the solvent over the solution, and p_0 is the vapor pressure of pure solvent. Substituting this value for a_1 in equation (68a) and forming the integral, we obtain

$$\int \partial ln a_2 = -\int \frac{N_1}{N_2}\partial ln \frac{p_1}{p_0}. \tag{95}$$

Since sufficiently accurate measurements of the vapor pressure cannot be made at low concentrations so that the activity coefficient of the solute may be determined, this equation is useful for determining activity ratios. To this end, the definite integral

$$\int_{a_2'}^{a_2''} \partial ln a_2 = -\int_{p_1'}^{p_1''} \frac{N_1}{N_2}\partial ln \frac{p_1}{p_0} \tag{96}$$

may be employed. By plotting $\frac{N_1}{N_2}$ against $ln\,\frac{p_1}{p_0}$ and evaluating the area between the limits graphically, the definite integral may be obtained. The negative of this integral equals $ln\,\frac{a_2''}{a_2'}$. [2]

That agreement between activity coefficients in the concentrated solutions calculated from the electromotive forces and the vapor pressures may be obtained is shown by Table XI. The values of the activity coefficient of potassium chloride in the second column were taken from Table IX, and those in

[1] Randall and Failey, *J. Am. Chem. Soc.*, **49**, 2678 (1927).
[2] Lewis and Randall, *J. Am. Chem. Soc.*, **43**, 1112 (1921).

the third column were computed by graphical integration of the data of Lovelace, Frazer, and Sease [1] by means of equation (96). The 1 molal values were assumed to be equal.

TABLE XI

ACTIVITY COEFFICIENTS OF POTASSIUM CHLORIDE FROM ELECTROMOTIVE FORCE AND VAPOR PRESSURE DATA

m	γ (E.M.F.)(25°)	γ (V.P.) (20°)
0.1	0.762	0.778
0.2	0.710	0.711
0.5	0.642	0.641
1.	(0.595)	(0.595)
2.	0.567	0.564
3.	0.569	0.562
4.	0.579	0.565

In the range from 0.2 to 4 molal the agreement is excellent. The values in the third column were obtained from data at 20° and at the higher concentrations are somewhat less than the values obtained from electromotive force data at 25°. A difference of this kind is to be expected as shown by Harned [2] from considerations of the magnitude and sign of the partial molal heat content of potassium chloride. Since in the solutions below 0.2 molal a small error in the vapor pressure measurement or in the graphical integration makes a considerable difference in the value of γ, the 0.1 molal agreement is not good.

Calculation of the Vapor Pressure and Activity of the Solvent from the Activity Coefficient of the Solute. van't Hoff's Factor, van't Hoff's Coefficient, and the Osmotic Coefficient: The vapor pressure of the solvent at all concentrations of the solute may be accurately calculated by the same method. Rearranging equation (68), we obtain

$$\partial ln a_1 = -\frac{N_2}{N_1}\partial ln a_2. \tag{68b}$$

In aqueous solutions

$$\frac{N_2}{N_1} = \frac{m}{55.5}. \tag{97}$$

Taking the logarithm of both sides of equation (51) which defines the activity coefficient of an electrolyte, we obtain

$$ln a_2 = \nu ln\gamma + \nu ln\left(\nu^{+\nu^+}\nu^{-\nu^-}\right)^{1/\nu} + \nu ln m, \tag{98}$$

since $a_\pm$ equals $a_2^{1/\nu}$. Upon differentiation of this equation, we obtain

$$\partial ln a_2 = \nu\partial ln\gamma + \nu\partial ln m. \tag{99}$$

[1] Lovelace, Frazer, and Sease, *J. Am. Chem. Soc.*, **43**, 102 (1921).
[2] Harned, *J. Am. Chem. Soc.*, **49**, 252 (1922).

Substituting (97) and (99) in (68*b*), we easily obtain

$$-\partial ln a_1 = \frac{m\nu}{55.5}(\partial ln m + \partial ln\gamma). \tag{100}$$

a_1 is proportional to the vapor pressure of the solution, p, and therefore upon fixing the proper limits, the integrals are

$$-\int_{p_0}^{p} \partial ln p = \frac{\nu}{55.5}\int_0^m \partial m + \frac{\nu}{55.5}\int_1^{\gamma} m\partial ln\gamma, \tag{101}$$

where p_0 is the vapor pressure of pure water.

Upon integration

$$ln\frac{p_0}{p} = \frac{m}{55.5}\left[\nu + \frac{\nu}{m}\int_1^{\gamma} m\partial ln\gamma\right]. \tag{102}$$

The term within the brackets is recognized to be van't Hoff's "i," whence equation (102) may be written

$$ln\frac{p_0}{p} = \frac{m}{55.5}[i]. \tag{103}$$

The expression within the brackets of equations (102) affords a simple means of evaluating van't Hoff's factor for an electrolyte from a knowledge of its concentration and activity coefficient, and, subsequently, the vapor pressure of the solution. Such a calculation can always be accomplished by graphical integration. Also when $ln\gamma$ is known as a function of m the integral may be evaluated. An illustration of this method has been given by Harned.[1]

The van't Hoff coefficient, γ_0, may be readily obtained from "i" by the equation defining it, which is,

$$\gamma_0 = \frac{i-1}{\nu-1}. \tag{104}$$

It is this coefficient which according to the classic theory of solutions of Arrhenius was considered to be a measure of the degree of dissociation.

For reasons of convenience, Bjerrum and Brönsted frequently employ the function, i/ν, which they call the osmotic coefficient, φ. The general differential equation which relates the activity coefficient and the osmotic coefficient may be readily obtained. Substituting $\nu\varphi$ for i in (103) and differentiating, we obtain

$$-\partial ln p = \frac{\nu\varphi}{55.5}\partial m + \frac{\nu m}{55.5}\partial\varphi. \tag{105}$$

But since $\partial ln p$ equals $\partial ln a_2$ this expression may be used to eliminate a_1 from

[1] Harned, *J. Am. Chem. Soc.*, **44**, 252 (1922); Taylor, Treatise on Physical Chemistry, Chap. XII, First Ed., Van Nostrand & Co., New York (1924).

equation (100). Thus we readily obtain

$$1 + m\frac{\partial ln\gamma}{\partial m} = \varphi + m\frac{\partial \varphi}{\partial m}. \tag{106}$$

We shall find that in very dilute solutions γ varies with the square root of the concentration according to the law

$$ln\gamma = -\beta m^{1/2}. \tag{107}$$

If we differentiate this expression with respect to m and substitute in (106) we obtain

$$\partial m - \tfrac{1}{2}\beta m^{1/2}\partial m = \partial(\varphi m). \tag{108}$$

which upon integration and resubstitution of (107) gives

$$-ln\gamma = 3(1 - \varphi). \tag{109}$$

From the value of $(1 - \varphi)$ obtained from (104), we find the relatively unimportant equation,

$$-lu\gamma = 3\left(\frac{\nu - 1}{\nu}\right)(1 - \gamma_0), \tag{110}$$

which shows the relation between van't Hoff's coefficient and the activity coefficient in very dilute solutions.

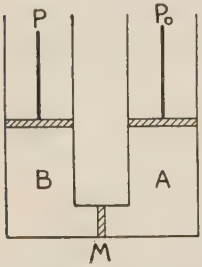

FIG. 9

Calculation of Osmotic Pressure: In the accompanying diagram (Fig. 9), A is a compartment containing pure solvent separated by a semipermeable membrane, M, from a compartment, B, containing the solution. Let the whole system be at constant temperature. Let P and P_0 be pressures such that the system is kept in equilibrium. The osmotic pressure, π, is defined by the difference in these pressures, or $(P - P_0)$. Thus, in compartment A, the solvent will be at a pressure P_0, and, in compartment B, the solvent in the solution will be at a pressure P.

Let us consider a process whereby a mol of solvent is reversibly transferred from the solvent to the solution through the osmotic membrane, and, as in the previous cases, let $\overline{F}_0$ and a_0 equal the partial free energy and activity of the pure solvent at an external pressure, P_0. The partial free energy and activity of the solvent in the solution at an external pressure P will also equal $\overline{F}_0$ and a_0, respectively, under the stipulated conditions of equilibrium. The free energy increment of such a process is zero. Let us now change the pressure on the solution from P to P_0. The change in activity of the solvent caused

by this change in pressure may be found by equation (67) which is

$$\left[\frac{\partial lna}{\partial p}\right]_T = \frac{\overline{V}_1}{RT}, \tag{67}$$

where $\overline{V}_1$ is the partial molal volume of the solvent. Rearranging this equation and forming the definite integral, we obtain

$$\int_{\overline{F}_0}^{\overline{F}_1} \partial \overline{F} = RT \int_{a_0}^{a_1} \partial lna = \int_{P}^{P_0} \overline{V}_1 \partial P, \tag{111}$$

where a_1 is the activity of the solvent in the solution at a pressure P_0. This equation is exact. If we neglect the change in $\overline{V}_1$ produced by a change in pressure, (the compressibility) $\overline{V}_1$ will equal the molal volume of the solvent V_0. Since the partial free energy of the pure solvent is zero, a_0 will equal unity, and

$$\overline{F}_1 = RTlna_1 = -\overline{V}_1(P - P_0) = -\pi V_0 \tag{112}$$

is obtained. If this equation be combined with (89), we obtain the well-known but approximate law

$$\pi = \frac{RT}{V_0} ln \frac{p_0}{p_1}, \tag{113}$$

which relates the osmotic pressure of the solution to the vapor pressure of the solvent. Combining (113) and (103), we obtain

$$\pi = \frac{RT}{V_0} \frac{m}{55.5} [i], \tag{114}$$

which at 25° reduces to

$$\pi = 24.42m[i], \tag{114a}$$

where π is in atmospheres.

Characteristics of Conductance Ratios, and the Thermodynamic Coefficients, and Some General Considerations Regarding the Classic Theory of Electrolytic Dissociation: van't Hoff introduced the factor i in the equation which expressed the abnormal freezing point lowering of solutions of electrolytes. Arrhenius recognized that only those solutions which possessed an i factor greater than unity conducted the electric current. As a result, he suggested that electrolytes were dissociated into ions, and that i was a measure of the total number of gram ions and mols which are produced by the dissociation of one mol of electrolyte. On this theory, if the process of ionization is a partial dissociation of molecules into ions, γ_0 is a degree of dissociation.

In order to measure the number of ions in a solution we turn to the electrical conductance. According to the classic ionic theory, the ions alone are the

carriers of electricity. If U_c and U_a are the mobilities of the cation and anion, respectively, the equivalent conductance, Λ, will be $\alpha\mathbf{F}(U_c + U_a)$, where α is the degree of dissociation. At infinite dilution, α equals unity and the equivalent conductance, Λ_0, equals $\mathbf{F}(U_c + U_a)$. Thus, $\frac{\Lambda}{\Lambda_0}$ will equal the degree of dissociation, or, more generally, the fraction of 1 gram equivalent existing as ions which are free to move through the solution at any concentration, only upon the assumption of Kohlrausch that the mobilities of the ions doe not change with the concentration, or that U_c equals U_c' and U_a equals U_a'. That the mobilities do not change with the concentration, that γ_0 and $\frac{\Lambda}{\Lambda_0}$ both measure the degree of dissociation and therefore should have the same value, are characteristics of the classic theory of electrolytic dissociation.

In Fig. 10, we plot values of $\frac{\Lambda}{\Lambda_0}$ as well as the values of the thermodynamic coefficients, γ, φ, and γ_0 of solutions of potassium chloride. All these quan-

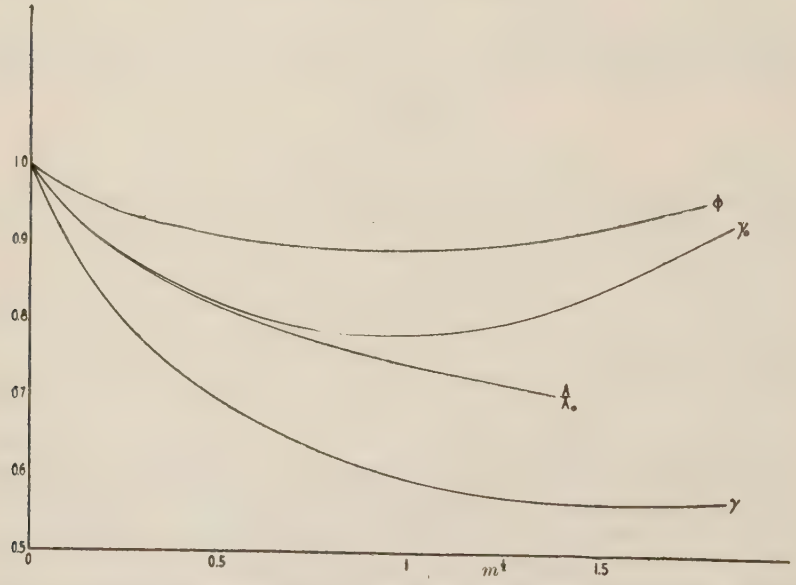

FIG. 10. Plots of Conductance Ratio, van't Hoff, Osmotic and Activity Coefficients of Potassium chloride

tities are defined in such a way that they equal unity at infinite dilution. γ, φ and γ_0 have been shown to be related by thermodynamics, and therefore a measurement of one of them is equivalent to that of another. They all, to a greater or less extent, show the characteristic minima. Of these coefficients, γ_0 approaches $\frac{\Lambda}{\Lambda_0}$ in magnitude, as m approaches zero, a fact which is true

for many electrolytes.[1] It is not strange therefore that in the classic theory of electrolytes, both γ_0 and $\frac{\Lambda}{\Lambda_0}$ were taken as a measure of α. More recent considerations show that these quantities are by no means related in so simple a manner.

Some General Considerations Regarding the More Recent Theories of Ionized Solutes: For many years, doubt has been raised as to whether any truly undissociated molecule exists in a dilute solution of typically strong electrolyte. Sutherland was the first to adopt a theory of complete dissociation. Noyes suggested an hypothesis of complete ionization but not complete dissociation for strong electrolytes, by which is meant that the ions which are not "free ions" are bound to ions of opposite sign by electrostatic forces. It is convenient to think of this as ionic association as distinguished from the formation of a truly undissociated molecule, a process which we may regard as involving a quantum jump. More recently, many investigators[2] have supported a similar theory.

The proponents of a theory of complete dissociation confront the task of accounting for the deviation of the conductance ratios and thermodynamic coefficients of electrolytes from unity solely by means of the electrostatic forces between the ions. Thus, Debye and Hückel[3] and Onsager[4] attempt to compute the variation of the mobilities of the ions with the concentration of the electrolyte from considerations involving the distribution of both positive and negative ions surrounding a given ion as it moves under the influence of an external field.

Let us reconsider equation (44) which defines the relative activity and equation (54) which expresses the law of an ideal solute. These are

$$\bar{F} = RT \ln a + \bar{F}_o \tag{44}$$

and

$$\bar{F}_c = RT \ln m + \bar{F}_0. \tag{54}$$

It is known that, in dilute solutions, equation (54) is almost exactly valid

[1] See the data of Noyes and Falk, *J. Am. Chem. Soc.*, **34**, 454 (1912); also Harned, Treatise on Physical Chemistry, Chap. XII, Table XVIII. 1st Edition. D. Van Nostrand Co., New York (1924).

[2] Sutherland, *Phil. Mag.*, (6) **3**, 167 (1902); **7**, 1 (1906); Noyes, *Congress Arts Sci., St. Louis Exposition*, **4**, 317 (1904); Bjerrum, *Proc. 7th Internat. Congr. Applied Chemistry*, Sect. X, London (1909); **16** *Skand. Naturforsk. Forhandl.* 1916, 226; *Z. Electrochem.*, **24**, 321 (1918); *Meddel. Kgl. Vet. Akad. Nobelinst.* **5**, Nr. 16, (1919); *Z. anorg. Chem.*, **109**, 275 (1920); *Z. physik. Chem.*, **104**, 406 (1923). Ghosh, *J. Chem. Soc.*, **113**, 449, 627, 707 and 790 (1918); *Trans. Farad. Soc.*, **15**, 154 (1919); *J. Chem. Soc.*, **117**, 823, 1390 (1920); *Z. physik Chem.*, **98**, 211 (1921); Hertz, *Ann. Physik*, (4) **37**, 1 (1912). Milner, *Phil. Mag.*, **23**, 551 (1912); **25**, 742 (1913); **35**, 214, 352 (1918); *Trans. Farad. Soc.*, **15**, 148 (1919). Debye and Hückel, *Physik. Z.*, **24**, 185, 305 (1923). Debye, *ibid.*, **24**, 334 (1923); **25**, 97 (1924). Hückel, *ibid.*, **26**, 93 (1925); Noyes, *J. Am. Chem. Soc.*, **46**, 1080 (1924).

[3] Debye and Hückel, *Physik. Z.*, **24**, 305 (1923).

[4] Onsager, *ibid.*, **28**, 277 (1927).

for an undissociated solute but is not valid for an electrolyte. The latter departure from validity is therefore due to ionization. This fact suggests that the partial free energy of an electrolyte may be divided into two parts, $\bar{F}_k$, the part associated with thermal free energy, and $\bar{F}_e$, the part associated with the electrical free energy. Thus, equation (44) may be written

$$\bar{F} = \bar{F}_c + \bar{F}_e = RTlnm + RTln\gamma + \bar{F}_0, \tag{115}$$

where $\bar{F}_c$ according to equation (54) which expresses the law of the ideal solute is given by

$$\bar{F}_c = RTlnm + \bar{F}_0.$$

The problem of calculating γ in very dilute electrolytic solutions from fundamental considerations regarding their nature, is resolved into the calculation of $\bar{F}_e$ since it is obvious that

$$\bar{F}_e = RTln\gamma. \tag{116}$$

This calculation has its analogue in the calculation of the effect of the forces of attraction and repulsion in the case of concentrated gases. Thus, van der Waal's equation is a result of the evaluation of the virial or force function and its effect on the pressure of a gas. In the present instance, our problem involves the electrostatic virial which is caused by the attraction of the ions according to Coulomb's forces, and their repulsion due to their size and to the solvent sheaths which surround them.

Such an attempt has been made by Milner but his method is very complicated and his calculations lead to a result which does not seem to be valid. The extraordinarily ingenious short cut due to Debye gives us for the first time a very close approximation to a valid solution of the problem of the behavior of very dilute solutions of strong electrolytes. We shall develop the most convincing aspects of this theory which have to do with the calculation of the activity coefficient.

The Limiting Law of the Theory of Debye and Hückel: Let us consider a solution containing s ions of valences

$$z_1 \cdots z_i \cdots z_s,$$

and let the numbers of each kind per cubic centimeter be

$$n_1 \cdots n_i \cdots n_s,$$

respectively. Take any ion of charge $z_i\epsilon$, where ϵ is the electronic charge, and consider an element of volume dV at a distance r from it according to Fig. 11. We shall consider the ions as point charges, a condition which is very closely

approached in very dilute solutions. We shall now proceed to determine the average potential, ψ, at the distance r from the ion under the conditions that the ions are point charges and that Coulomb's forces, or electrostatic forces which vary inversely as the square of the distance, are operative.

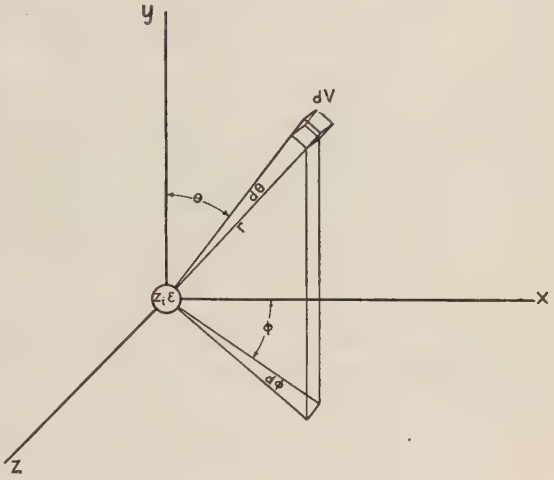

FIG. 11

Owing to their thermal motion, ions of different kinds will be passing in and out of the volume element, dV. Sometimes there will be an excess of positive, sometimes negative charges in the element. If, however, we take the time integral of the charge in the element and divide by the whole time, we obtain the mean charge of the element. This will be equal and opposite in sign to the charge on the central ion. Thus, we see that the central ion is surrounded by an "ionic atmosphere" of opposite sign, and between this ionic atmosphere and the potential of the central ion, there will exist a difference in potential. Debye and Hückel now proceed to evaluate this potential by the combined use of Boltzmann's and Poisson's equations.

According to Boltzmann's principle of distribution, the average number of ions of the ith kind in the element of volume will be

$$n_i e^{-z_i(\epsilon\psi/kT)} dV, \tag{117}$$

their density,

$$n_i e^{-z_i(\epsilon\psi/kT)} \tag{118}$$

and, consequently, the average electrical density ρ_i will be

$$\rho_i = n_i z_i \epsilon e^{-z_i(\epsilon\psi/kT)}. \tag{119}$$

The total electrical density of all ions will therefore be

$$\rho = \epsilon \sum_1^s n_i z_i e^{-z_i(\epsilon\psi/kT)}. \tag{120}$$

e is the base of the natural logarithms, and k is Boltzmann's constant.

The electrical density of the element of volume is also related to the potential at a distance r from the ion by Poisson's equation.[1] First let us consider the equipotential surface represented by ψ_1, in Fig. 12, produced by some field of force. The magnitude of the force normal to the surface ψ_1, will obviously be $\frac{\partial \psi}{\partial n}$ if n is a distance taken normal to the surface; n may be in any direction in a space of three dimensions. In order to use this expression for evaluating the normal force from the potential it is convenient to use a differential operator, ∇, which enables us to express this relation generally and which later may be expressed in terms of the usual co-ordinates as for example x, y, z, or γ, θ, φ, etc. Thus, if we operate on the potential with ∇, we obtain the force normal to the equipotential surface. This is called the gradient of the potential, or grad ψ. Thus

FIG. 12

$$\boldsymbol{F} = grad\ \psi = \nabla\psi = \bar{n}_1 \frac{\partial \psi}{\partial n}, \tag{121}$$

where $\boldsymbol{F}$ is the force and $\bar{n}_1$ is a unit vector normal to the surface ψ_1 and gives $\partial\psi/\partial n$ the vectorial character of a force. Now, let us consider any surface containing an electrical charge density equal to ρ which is represented in cross section in Figure 13(a). From this surface there will be a total outward

FIG. 13

flux per unit volume of the lines of force. This we denote the divergence of the force, and

$$div\ \boldsymbol{F} = div\ grad\ \psi = \nabla \cdot \nabla\psi. \tag{122}$$

If no lines of force originate within the surface, and if this surface lies in a force field, as many lines of force enter as leave it and the total outward flux equals zero or $div\ \boldsymbol{F} = 0$ (Fig. 13b). Thus, when the differential operator, ∇, or nabla is applied in a certain way upon $\nabla\psi$, it gives the total outward flux of the force. Now, when we consider a field subject to Coulomb's forces

[1] Coffin, Vector Analysis, p. 143, 2nd edition, John Wiley and Co., New York (1911). Houston, An Introduction to Mathematical Physics, p. 20, Longmans, Green & Co., London (1912). Haas, Vector analysis, Gruyter & Co., Berlin and Leipzig (1922).

such as is represented by Fig. 13*a*, we find that

$$\nabla \cdot \nabla \psi = -\frac{4\pi\rho}{D}, \tag{123}$$

where D is the dielectric constant of the medium. This is Poission's equation and simply states that the total outward flux of force from our volume element is equal to $-4\pi/D$ times the density of electrification within the element.

We are now interested in computing the relation of the potential to a quantity which is proportional to the square root of the concentration. If we substitute the value for ρ which was found by Boltzmann's distribution law in equation (123), we obtain

$$\nabla \cdot \nabla \psi = -\frac{4\pi\epsilon}{D} \sum_{1}^{s} n_i z_i e^{-z_i(\epsilon\psi/kT)}. \tag{124}$$

In the cases of solutions containing electrolytes of symmetrical valence types such as KCl, $MgSO_4$, etc., this equation becomes

$$\nabla \cdot \nabla \psi = -\frac{4\pi\epsilon}{D} \sum_{1}^{s} n_i z_i \left[e^{-z_i(\epsilon\psi/kT)} + e^{z_i(\epsilon\psi/kT)} \right]$$

or

$$\nabla \cdot \nabla \psi = 4\pi\epsilon \sum_{1}^{s} n_i z_i \sinh \frac{z_i \epsilon \psi}{kT} \tag{125}$$

where the hyperbolic sine replaces the exponential form. In the cases of ions of unsymmetrical valence types, this is not strictly true. Since the expansion of equation (124) is accompanied by great difficulties,[1] we shall employ (125) with the proviso that it may not be expected to hold rigidly for solutions containing ions of mixed valence types. Since $z_i\epsilon\psi/kT$ is small, it may replace $\sinh z_i\epsilon\psi/kT$ without appreciable error whence we obtain

$$\nabla \cdot \nabla \psi = \frac{4\pi\epsilon^2}{DkT} \sum_{1}^{s} n_i z_i^2 \psi. \tag{126}$$

Now let

$$\kappa^2 = \frac{4\pi\epsilon^2}{DkT} \sum_{1}^{s} n_i z_i^2 \tag{127}$$

and, therefore, (126) may be written

$$\nabla \cdot \nabla \psi = \kappa^2 \psi. \tag{128}$$

$\nabla \cdot \nabla \psi$ may now be expressed in spherical co-ordinates and owing to the uniform distribution of the ions about the central ion (Fig. 11) ψ will depend on r and not on θ and φ. Thence, we obtain

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) = \kappa^2 \psi. \tag{129}$$

[1] Müller, *Physik. Z.*, **28**, 324 (1927); Gronwall, LaMer and Sandved, *ibid.*, **29**, 358 (1928).

The general integral of this equation is

$$\psi = \frac{Ae^{-\kappa r}}{r} + \frac{A'e^{\kappa r}}{r}, \tag{130}$$

where A and A' are integration constants. Now, ψ must approach zero, as r increases indefinitely, and therefore A' must equal zero. The potential of a point charge ϵ in a medium of dielectric constant D is

$$\psi = \frac{\epsilon}{D}\frac{1}{r}. \tag{131}$$

This is the case when the concentration is zero, or when κ equals zero. Hence,

$$\psi_i = \frac{A}{r} = \frac{z_i\epsilon}{Dr} \tag{132}$$

when κ equals zero, A equals $z_i\epsilon/D$ and our equation (103) for the potential of the ion becomes

$$\psi = \frac{z_i\epsilon}{D}\frac{e^{-\kappa r}}{r}, \tag{133}$$

which can be written

$$\psi = \frac{z_i\epsilon}{D}\frac{1}{r} - \frac{z_i\epsilon}{D}\frac{1 - e^{-\kappa r}}{r}. \tag{133}$$

The first member on the right is simply the potential of the ion in a medium of dielectric constant, D, when it is uninfluenced by other ions. This potential is independent of the concentration and therefore does not interest us. The second member is the desired potential and represents the potential of the ion caused by its ionic atmosphere. For small values of r, $(1 - e^{-\kappa r}/r)$ equals κ since upon development in series $(1 - e^{-\kappa r})$ equals κr for small values of r, and therefore

$$\psi = -\frac{z_i\epsilon\kappa}{D}. \tag{134}$$

Thus, $1/\kappa$ in Debye and Hückel's theory functions in a manner similar to r in equation (131).

κ has the dimensions of a reciprocal length and is a very significant quantity in this theory. From equation (127) which defines it, $1/\kappa$ is found to be given by

$$\frac{1}{\kappa} = \frac{3.06 \times 10^{-8}}{\sqrt{c}}\text{ cm.} \tag{135}$$

in the case of a uniunivalent electrolyte in water at 0° if c is expressed in mols per liter. Thus in a normal solution, $1/\kappa$ has molecular dimensions. Further, let us examine the relation of κ to the electrical density at a distance r from

the ion. From equations (123), (128) and (133) we easily obtain

$$\rho = -\frac{\kappa^2 z_i \epsilon e^{-\kappa r}}{4\pi r}, \tag{136}$$

which gives the decrease in density with the increase in distance. $1/\kappa$ is called the radius of the ionic atmosphere by Debye and Hückel.

The knowledge of the potential of the ion given by equation (134) may now be employed to evaluate the thermodynamic coefficients. To do this, it is most convenient to consider the reversible discharge of the ion at constant concentration, or constant κ. This would be similar to the reversible discharge of an ion on an electrode, and is similar to the discharge of a condenser. Since κ is constant, the potential is proportional to the charge. The work done by such a process is the free energy change of the discharge of the ion and is therefore equal to

$$\bar{F}_i = \int_0^{\psi} z_i \epsilon d\psi = \int_0^{\psi} a\psi d\psi = \frac{a\psi\psi}{2} = \frac{z_i \epsilon \psi}{2} = -\frac{(z_i\epsilon)^2 \kappa}{2D}, \tag{137}$$

where a is the factor of proportionality. According to equation (116), $\bar{F}_i$ will be given by

$$\bar{F}_i = kTln\gamma_i \tag{116a}$$

and

$$ln\gamma = -\frac{(z_i\epsilon)^2 \kappa}{2Dkt}. \tag{138}$$

These very important considerations give us an insight into the meaning of the activity coefficient and the mechanism of a concentration cell. Thus, in very dilute solutions, in which the ions may be considered as point charges the logarithm of the γ ratio measured by a concentration cell is proportional to the sum of work of the reversible discharge of one ion in one solution and work of the reversible charging of the ion in the other solution. That there exists a difference in electrical free energies in these two solutions depends on the peculiarity of the distribution of the ionic atmosphere in two solutions.

Substituting the value of κ^2 given by (127) in (137) we obtain

$$ln\gamma_i = -\frac{(z_i\epsilon)^2}{2DkT}\sqrt{\frac{4\pi\epsilon^2}{DkT}\sum_1^s n_i z_i^2} \tag{139}$$

for the general limiting law for the activity coefficient of an ion. The general formula for the activity coefficient product of all s ions is

$$ln\gamma = \frac{1}{\sum_1^s \nu_i} ln\gamma_1^{\nu_1} \cdots \gamma_i^{\nu_i} \cdots \gamma_s^{\nu_s}, \tag{140}$$

which upon substitution of the values for γ_1, γ_2, etc., given by equation (139), gives

$$ln\gamma = -\frac{\sum_1^s \nu_i z_i^2}{\sum_1^s \nu_i} \frac{\epsilon^2}{2DkT} \sqrt{\frac{4\pi e^2}{DkT} \sum_1^s n_i \frac{\sum \nu_i z_i^2}{\sum \nu_i}}$$

$$= -\left(\frac{\sum_1^s \nu_i z_i^2}{\sum_1^s \nu_i} \right)^{3/2} \left(\frac{\pi^{1/2} \epsilon^3}{D^{3/2} k^{3/2} T^{3/2}} \right) \sqrt{\sum_1^s n_i} \qquad (141)$$

In this equation, ϵ equals 4.774×10^{-10} electrostatic units, k equals 1.372×10^{-16} ergs, and since $\sum n_i$ equals $n \sum \nu_i$ and n is the number of molecules of electrolyte dissociating into ions in a cubic centimeter, it equals $6.06 \times 10^{-20} c$, where c is the concentration of the electrolyte which produces the ith ion in mols per 1000 cc. solution. Upon substitution of these values in (141), we obtain

$$ln\gamma = -\left(\frac{\sum_1^s \nu_i z_i^2}{\sum_1^s \nu_i} \right)^{3/2} \frac{2.954 \times 10^6}{D^{3/2} T^{3/2}} \sqrt{\sum_1^s c\nu_i} \qquad (142)$$

This equation contains three important relations.

1. The logarithm of the activity coefficient varies with the square root of the concentration.

2. The logarithm of the activity coefficient is inversely proportional to the three-half power of the dielectric constant.

3. The factor which determines the effect of the different valences of ions is given by $\left(\frac{\sum_1^s \nu_i z_i^2}{\sum_1^s \nu_i} \right)^{3/2}$.

Since we are chiefly interested in the activity coefficient of an electrtolye dissociating into two ions, we evaluate

$$ln\gamma = \frac{1}{\nu} ln\gamma_1^{\nu_1} \gamma_2^{\nu_2} \qquad (143)$$

by the use of equations (139) and (142), and obtain

$$ln\gamma = -\left(\frac{\sum_1^2 \nu_i z_i^2}{\sum_1^2 \nu_i} \right) \frac{2.954 \times 10^6}{D^{3/2} T^{3/2}} \sqrt{\sum_1^s c\nu_i z_i^2}. \qquad (144)$$

Note that in the valence factor the summation is for the two kinds of ions produced by the dissociation of the electrolyte which as the activity coefficient γ while the summation under the square root is for all the ions. This is important since it is seen that the equation will be valid for the activity coefficient of the electrolyte either in the pure solvent or in a solvent containing other ions of s different kinds. Since, in the case of an electrolyte, dissociating into two ions $\frac{\sum_1^2 \nu_i z_i^2}{\sum_1^2 \nu_i}$ equals $z_1 z_2$ equation (144) may be written in the form

$$ln\gamma = -\frac{2.954 \times 10^6}{D^{3/2}T^{3/2}} z_1 z_2 \sqrt{\sum c_i z_i^2}. \qquad (145)$$

If we let c which is in mols per liter equal m in mols per 1000 gs. solvent, a justifiable procedure for very dilute solutions, we obtain

$$ln\gamma = -\frac{2.954 \times 10^6}{D^{3/2}T^{3/2}} z_1 z_2 \sqrt{2\mu}. \qquad (146)$$

since, according to (85), $\sum m_i z_i^2$ equals 2μ.

We shall consider first the equations for aqueous solutions. Upon substituting the values 87.8 and 78.8 for the dielectric constant of water at 0° and 25°, respectively,[1] in equation (146) we obtain the very simple equations

$$\left.\begin{aligned} \log\gamma &= -0.489 z_1 z_2 \sqrt{\mu} \quad \text{at } 0°; \\ \log\gamma &= -0.504 z_1 z_2 \sqrt{\mu} \quad \text{at } 25°. \end{aligned}\right\} \qquad (147)^2$$

General Experimental Considerations: Noyes and Falk [3] showed from the freezing point data available at that time, that in the case of a uniunivalent electrolyte, the equation

$$2 - i = k\sqrt[3]{m}$$

expressed within the experimental error the variation of i, the van't Hoff factor, with the concentration in moderately dilute solutions. Bjerrum [4] showed that this expression was equivalent to

$$\log\gamma = -\beta\sqrt[3]{m}.$$

Further, the cube root law followed from the theory of Ghosh. Lewis and Linhart employed a function which was equivalent to

$$\log\gamma = -\beta m^{\alpha}. \qquad (80)$$

Lewis and Randall,[5] upon examining the available freezing point data suggested

[1] Noyes, *J. Am. Chem. Soc.*, **46**, 1098 (1924). Drude, *Ann. Physik*, **59**, 61 (1896).
[2] Brönsted and LaMer, *J. Am. Chem. Soc.*, **46**, 555 (1924).
[3] Noyes and Falk, *J. Am. Chem. Soc.*, **32**, 1011 (1910).
[4] Bjerrum, *Z. Electrochem.*, **24**, 321 (1918); *Z. anorg. Chem.*, **109**, 275 (1920).
[5] Lewis and Randall, Thermodynamics, p. 345, McGraw-Hill Book Co., New York (1923).

that for uniunivalent electrolytes α' equals $\frac{1}{2}$ but obtained values differing considerably from $\frac{1}{2}$ for electrolytes of other valence types. Brönsted employed the equation

$$\log \gamma = -\beta\sqrt{m}$$

as a universal limiting function for all types of electrolytes. That such a function would follow from Milner's theory has been shown by Cavanaugh.[1]

There seems to be little doubt that the square root law is correct, since it is a direct consequence of the operation of Coulomb's forces. On the other hand, the experimental proof is by no means easy since it is necessary to have accurate data in regions of very low concentrations. The limiting equation of the theory of Debye and Hückel was deduced upon the assumption that the ions were electrically charged mass points. This condition only approaches validity at very low concentrations. At higher concentrations, effects due to the actual sizes of the ions, their water sheaths, possible ion association, possible changes in dielectric constants, and repulsive forces between the ions become operative. Nevertheless, sufficient evidence has been obtained from various sources to show that in very dilute solutions the square root law is valid.

To verify their limiting law, Debye and Hückel employed all the available freezing point data, and found that as the concentration approached zero, these data appeared generally to approach the values required by the theory. These results cannot be said to establish the law completely, nor can the calculations of freezing point, and solubility data by Noyes.[2] Unquestionably, the best direct evidence so far obtained for the theory comes from the solubility measurements of slightly soluble higher order cobalt compounds which have been made by Brönsted and his collaborators. Also, a striking agreement has been recently obtained by Bray[3] who measured the activity coefficient of zinc sulphate in aqueous solutions by the electromotive force method. This is a particularly good example since according to equation (147) in the case of a bibivalent salt, $\log \gamma = -4\sqrt{m}$, and, consequently, varies very rapidly with the salt concentration.

In non-aqueous solvents, direct evidence has not been obtained for the limiting law.[4] Woolcock and Hartley are of the opinion that in ethyl and methyl alcohol solutions hydrochloric acid is not completely dissociated.

As a result of these and many other studies,[5] we may summarize the present status of the theory as follows:

1. In the case of typical strong electrolytes in aqueous solutions, a general agreement is obtained and no striking departures are noticeable. In all cases, the square root law is valid.

[1] Cavanaugh, *Phil. Mag.*, **43**, 606 (1922); **44**, 226 (1922); **44**, 610 (1922).
[2] Noyes, *J. Am. Chem. Soc.*, **46**, 1098 (1924).
[3] Bray, *J. Am. Chem. Soc.*, **49**, 2372 (1927).
[4] Woolcock and Hartley, *Phil. Mag.*, [7], **5**, 1133 (1928).
[5] Noyes and Baxter, *J. Am. Chem. Soc.*, **47**, 2122 (1925); Scatchard, *ibid.*, **47**, 2098 (1925).

2. The work of Brönsted and his collaborators on the solubility of salts in salt solutions affords excellent evidence for the validity of equation (147), particularly in regard to the square root law and the valence factor.

Activity Coefficients of Electrolytes in Salt Solutions from Solubility Data: We have found as a general thermodynamical principle that, when a system of more than one phase at constant pressure and temperature is in equilibrium with another phase, the activity of any component is the same in each phase. If, then, we have a salt in equilibrium with its saturated solution, the activity of the solid equals the activity of the salt in the saturated solution. At constant pressure and temperature, the activity of the solid will be a constant, k'. Consequently, under these conditions

$$k' = a_+^{\nu+} a_-^{\nu-} = \gamma_+^{\nu+} \gamma_-^{\nu-} (\nu_+ m_+)^{\nu+} (\nu_- m_-)^{\nu-}, \tag{148}$$

where $(\nu_+ m_+)$ and $(\nu_- m_-)$ are the molalities of the ions. Since γ equals $(\gamma_+^{\nu+} \gamma_-^{\nu-})^{1/\nu}$ we obtain

$$k = \gamma (\nu_+^{\nu+} \nu_-^{\nu-})^{1/\nu} (m_+^{\nu+} m_-^{\nu-})^{1/\nu}. \tag{149}$$

A salt may be dissolved in a salt solution which does not contain ions common with that of the dissolved salt, or in one which contains a common anion or cation. In the case of the first or heteroionic solvent, the molal solubility, S, equals m_+ or m_- and therefore equation (149) becomes

$$k = \gamma (\nu^{+\nu+} \nu^{-\nu-})^{1/\nu} S. \tag{150}$$

Now, let S_0 and γ_0 equal the solubility and activity coefficient in the saturated solution of the salt in the solvent not containing other salts, and S and γ equal the same quantities in the salt solutions. Then, from (150), we easily obtain

$$\frac{S_0}{S} = \frac{\gamma}{\gamma_0}. \tag{151}$$

This exact and general relation is valid for solutions of all strengths. In the case of very dilute solutions, we may apply the limiting equation (147), and obtain

$$\log \frac{S_0}{S} = -0.5 z_1 z_2 (\sqrt{\mu} - \sqrt{\mu_0}). \tag{152}$$

If we define an ideal solubility, S_∞, corresponding to unit value of γ at infinite dilution, we may obtain

$$\log \frac{S_\infty}{S} = -0.5 z_1 z_2 \sqrt{\mu}. \tag{153}$$

In the case of a homoionic solvent with an anion common to that of the dissolved salts, the solubility, S, equals m_+, and therefore we obtain from equation (149),

$$k = \gamma (\nu^{+\nu+} \nu^{-\nu-})^{1/\nu} (S^{\nu+} m_-^{\nu-})^{1/\nu} \tag{154}$$

and, consequently,

$$\frac{\nu^+}{\nu}\log\frac{S_0}{S}+\frac{\nu^-}{\nu}\log\frac{m_0}{m_-}=\log\frac{\gamma}{\gamma_0}, \tag{155}$$

where the subscripts have the same significance as in equation (151). When the cation is common,

$$\frac{\nu^-}{\nu}\log\frac{S_0}{S}+\frac{\nu^+}{\nu}\log\frac{m_0}{m_+}=\log\frac{\gamma}{\gamma_0} \tag{155a}$$

is obtained.

The classic investigations on this subject begun by Noyes, and followed by the papers of Noyes and Bray, Bray and Winninghoff, Harkins and Winninghoff, Harkins and Paine, and Harkins and Pearce[1] have been dis-

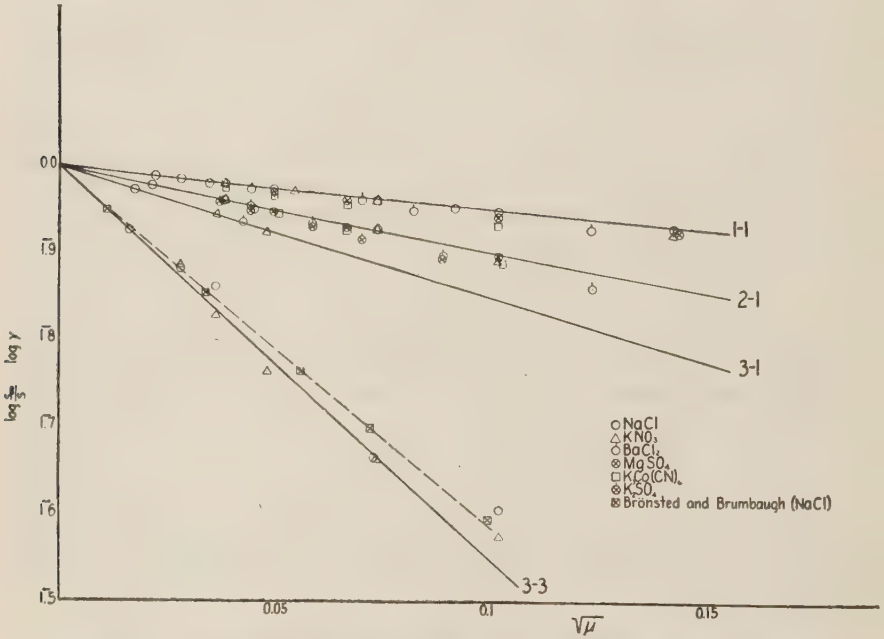

FIG. 14. Experimental Verification of the Limiting Equation of the Debye and Hückel Theory from Solubility Data

Saturating Salt

1–1 $[Co(NH_3)_4C_2O_4]^I[Co(NH_3)_2(NO_2)_2C_2O_4]^I$
2–1 $[Co(NH_3)_4C_2O_4]_2^I[S_2O_6]^{II}$
3–1 $[Co(NH_3)_6]^{III}[Co(NH_3)_2(NO_2)_2C_2O_4]_3^I$
3–3 $[Co(NH_3)_6]^{III}[Fe(CN)_6]^{III}$
3–3 $[Co(NH_3)_6]^{III}[Co(CN)_6]^{III}$

[1] A. A. Noyes, *Z. physik. Chem.* (1890); Noyes and Bray, *J. Am. Chem. Soc.*, **30**, 1643 (1908); Bray and Winninghoff, *ibid.*, **33**, 1663 (1911); Harkins and Winninghoff, *ibid.*, **33**, 1827 (1911); Harkins and Paine, *ibid.*, **41**, 1155 (1919); Harkins and Pearce, *ibid.*, **38**, 2679 (1916).

cussed by Lewis and Randall, and more particularly in relation to the Debye and Hückel theory by Noyes.[1] The solubilities of the salts employed in these studies were somewhat too great for an exact test of the theory. Brönsted and his collaborators have, however, overcome this difficulty by finding methods for determining the solubilities of many higher order cobalt compounds in salt solutions, and were thus able to investigate equation (147) in the region of 0.00005 to 0.1 total molalities. In Fig. (14), we plot some of the results obtained by Brönsted and LaMer, Brönsted and Brumbaugh and LaMer, King, and Mason.[2] Log γ or log $\frac{S_\infty}{S}$ is plotted against $\sqrt{\mu}$. The solid lines are the theoretical curves obtained by equation (147) for uniuni-valent (1–1), biunivalent (2–1), triunivalent (3–1), and tritrivalent (3–3) salts. The dashed line represents the results obtained by Brönsted and Brumbaugh. The agreement between the observed and theoretical results is indeed excellent considering the number and character of the solvent salt solutions which were employed. In the case of the 3–3 salt, Brönsted and Brumbaugh obtained 0.46 instead of 0.50 for the constant in the theoretical equation (147).

Considerable difficulties are encountered, however, in the cases of solutions of 3–1 salts in solvents containing electrolytes of mixed valence types as shown by the recent work of LaMer and Mason. When the solvent salt possessed polyvalent ions, wide deviations from the theoretical equation were obtained even at total concentrations as low as 0.0005μ. We have already pointed out that for such solutions, the substitution of the hyperbolic sine in equation (125) for the expression in equation (124) was not justifiable. LaMer and Mason think that the cause of the discrepancy is due to neglecting the higher terms of the expansion of equation (124). This very difficult problem has been attacked with considerable success by Gronwall, LaMer, and Sandved, and by Müller.[3] Indeed, it may be necessary to abandon the method of calculation of the electrostatic virial employed by Debye and Hückel, and find some other method similar perhaps to the method of Milner in order to obtain a general solution of the problem.

The Effect of the Apparent Diameters of the Ions, and the Probability of Ionic Association: The limiting equation of the theory of Debye and Hückel is only to be expected to be strictly valid at infinite dilution. The first thing to consider in an attempt to meet the conditions of a real solution at moderate concentration is the effect of the size of the ions on the potential. Since the actual sizes of the ions prevent their charges from coming together, the net effect will be similar to a repulsive force, and since the attractive forces have been shown to decrease the activity coefficient, this effect will tend to increase them. Debye and Hückel have made this calculation but the deduction is too

[1] Noyes, *J. Am. Chem. Soc.*, **46**, 1098 (1924).

[2] Brönsted and LaMer, *J. Am. Chem. Soc.*, **46**, 555 (1924); Brönsted and Brumbaugh, *ibid.*, **48**, 2015 (1926); LaMer, King and Mason, *ibid.*, **49**, 363 (1927).

[3] LaMer and Mason, *J. Am. Chem. Soc.*, **49**, 410 (1927); Grunwall, LaMer, and Sandved, *Physik. Z.*, **29**, 358 (1928); Müller, *Physik. Z.*, **28**, 324 (1927); **29**, 78 (1928).

complicated to be given in this discussion. They obtain the equation

$$\log \gamma = -\frac{0.356 z_1 z_2 \sqrt{\Gamma}}{1 + A\sqrt{\Gamma}}, \tag{156}$$

in which Γ equals $\sum_1^s c_i z_i^2$ and A is a constant which is related to the "apparent ionic diameter," or the mean value of the distance, a, which a positive or negative ion can approach another ion by the equation,

$$A = 0.232 \times 10^8 \times a. \tag{157}$$

The constant A differs for different electrolytes and will be shown to be of the correct order of magnitude. The above equation is a considerable improvement over the limiting equation for the calculation of γ in regions of concentration from 0.005 to 0.1 molal but does not account for the behaviors of more concentrated solutions.

The Debye and Hückel theory is based on the theory of complete dissociation, and does not include the possibility of the removal of ions by electrical association. The probability of such electrical combination between ions of opposite sign would be expected to be proportional to the probability that the two ions in question actually touch. The variation of the probability as a function of the distance between the ionic charges has been investigated by Bjerrum [1] by the use of the Boltzmann principle. He finds that this probability first diminishes, then passes through a minimum, and finally increases upon the decrease of the distance. Thus, solutions which contained positive and negative ions of radii such that their sum corresponded to the minimum probability would associate the least. With either larger or smaller sums of ionic radii greater association would be expected. This important consideration has not yet been completely elucidated. Indeed, more must be known about the effect (on the possibility of such association) of the presence of solvent sheaths which unquestionably surround the ions.

Besides the ionic diameter, the amount of ionic association and also the amount of undissociated molecules formed will depend on the kind of ion under consideration, or its fine structure. Indeed, the difference in behavior between the activity coefficients of the alkali halides and their corresponding hydroxides previously shown in Figs. 6 and 7 would indicate that the unsymmetrical hydroxide ion has a greater tendency to combine with sodium and lithium ions than has the chlorine ion which has a "noble gas type" electron structure.[2]

Form of the Activity Coefficient-Concentration Function at High Concentrations and at Constant Temperature and Pressure: By adding a simple linear term containing the constant α to equation (80) which gives

$$\log \gamma = -\beta m^{\alpha'} + \alpha m, \tag{158}$$

[1] Bjerrum, *Det Kgl. Danske Videns, Selskab.* VII, 9 (1926).

[2] Harned, *J. Am. Chem. Soc.*, **47**, 676 (1925); *Z. physik. Chem.*, **117**, 1 (1925); *Trans. Farad. Soc.*, **23**, 462 (1927).

Harned [1] has shown that the activity coefficients of many electrolytes may be computed with considerable accuracy through the concentration range from 0.001 to 3 molal. Further, by the use of equations (68) and (158), he has shown that van't Hoff's coefficients, γ_0, may be conveniently computed.

Recently, Hückel [2] has obtained the equation

$$\log \gamma = -\frac{0.356 z_1 z_2 \sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} + B\Gamma - \log (1 + 0.018\nu m), \tag{159}$$

in which B is a constant, and the logarithmic term is merely employed to change $\log f$ to $\log \gamma$ where $\log f$ is equal to the mean activity of the electrolyte divided by its mol fraction. This equation contains the linear term used by Harned, added to equation (156) of the original Debye and Hückel theory. The linear term was derived from theoretical considerations which involve the change in dielectric constants with the change in concentration. This result was deduced from the assumption that the dielectric constant of the medium varied linearly with the concentration according to the equation

$$D = D_0 - \sum_1^s \delta_i c_i, \tag{160}$$

where D_0 is the dielectric constant of the solvent, δ_i is a constant characteristic of an ion, c_i is the concentration in mols per liter of solution. The summation is for all the ions present. The introduction of equation (160) in the theory led to a very complicated expression which Hückel showed to be very nearly equivalent to the linear term $B\Gamma$.

Although the variation in the dielectric constant of the medium is very probably a factor which must be considered in the treatment of concentrated solutions, it is certainly not the only one. It is best at the present time to regard the linear term in equation (159) as empirical.

The nature of the functions expressed by the limiting equations (147), equation (156) which includes the apparent ionic diameters, and equation (159), as applied to the activity coefficients of uniunivalent electrolytes is shown in Fig. 15. By comparison of the plots of equation (159) using the different values of B with the results for the uniunivalent halides given in Fig. 6, it is evident that this function expresses in a general way the observed results. This equation has been tested by Hückel, Scatchard, Harned, Harned and Åkerlöf, Harned and Douglas, and Lucasse [3] with data obtained in the case of many electrolytes in aqueous and in some non-aqueous solutions and has been shown by them to be valid within narrow limits. This equation affords a powerful means of extrapolation to dilute solutions from accurate

[1] Harned, *J. Am. Chem. Soc.*, **42**, 1808 (1920); **44**, 252 (1922); Chap. XII, Taylor, Treatise on Physical Chemistry, 1st Edition, p. 744 et seq. Van Nostrand & Co., New York, 1924.

[2] Hückel, *Physik. Z.*, **26**, 93 (1925).

[3] Hückel, *Physik. Z.*, **26**, 93 (1925); Scatchard, *J. Am. Chem. Soc.*, **47**, 2098 (1925); Harned, *ibid.*, **48**, 326 (1926); Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926); Harned and Douglas, *J. Am. Chem. Soc.*, **48**, 3095 (1926); Lucasse, *Z. physik. Chem.*, **121**, 254 (1926); Harned, *J. Am. Chem. Soc.*, **51**, 416 (1929).

data obtained at high concentrations. The method of extrapolation is given in detail in Hückel's contribution. In Table XII are given the observed and calculated activity coefficients computed by this means for a few typical electrolytes. At the bottom of the table are given the values of the constants, A and B, and also the values obtained for the mean distance of approach, a. The calculated results agree with the observed quite well. The maximum deviation in the case of hydrochloric acid in the range of concentration from 0.001 to 1 molal is 0.24 per cent, in the case of sodium chloride from 0.001 to 3 molal 0.6 per cent. The strontium chloride calculation is an average one for a biunivalent salt. In this case, the experimental results are not as accurate. Although as we previously pointed out, the activity coefficients of the hydroxides compared with the halides were somewhat peculiar, they can be calculated with considerable accuracy by the above method.

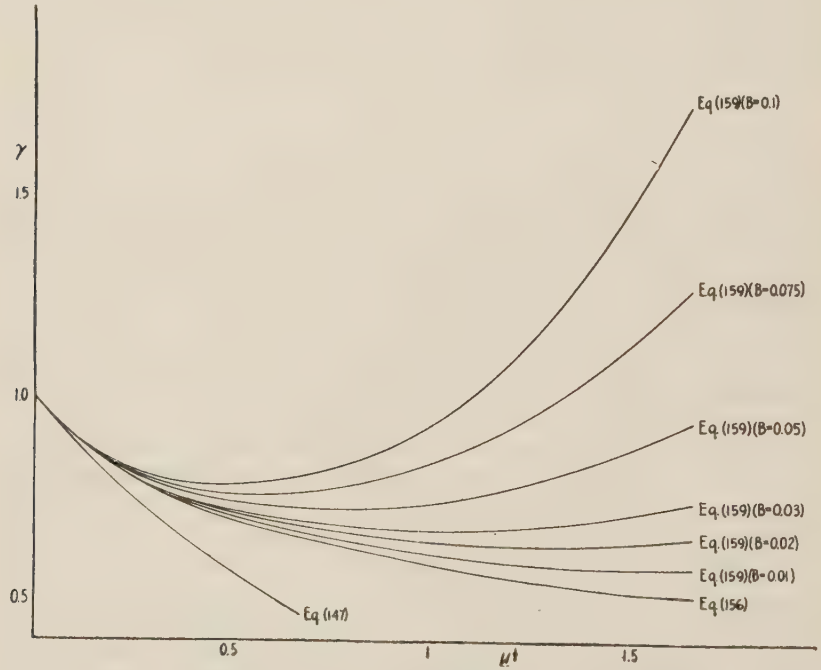

FIG. 15. Illustration of the Functions of the Debye-Hückel Theory

Activity Coefficients of Electrolytes in Salt Solutions from Electromotive Force Data: We have developed the general method of the determination of the activity coefficients of electrolytes in salt solutions from solubility measurements. This important method is limited, however, to the saturated solution of the electrolyte in question. Electromotive force measurements may sometimes be employed for the same purpose and when this is possible the activity coefficient of an electrolyte at different concentrations may be determined in salt solutions of different concentrations.

TABLE XII

OBSERVED AND CALCULATED ACTIVITY COEFFICIENTS IN CONCENTRATED SOLUTIONS

HCl [1]			NaCl [2]		
m	γ obs.	γ calc.	m	γ obs.	γ calc.
0.001	0.965	0.966	0.001	0.966	0.965
0.005	0.928	0.929	0.005	0.928	0.928
0.01	0.904	0.905	0.01	0.903	0.903
0.05	0.829	0.831	0.05	0.821	0.819
0.1	0.796	0.795	0.1	0.778	0.775
0.2	0.766	0.766	0.2	0.732	0.729
0.5	0.757	0.757	0.5	0.678	0.678
1.	0.810	0.811	1.	0.656	0.658
1.5	0.903	0.896	1.5	0.658	0.662
			2.	0.670	0.674
			2.5	0.690	0.692
			3.	0.714	0.715
			3.5	0.749	0.739
			4.0	0.779	0.764

$SrCl_2$ [3]			NaOH [4]		
m	γ obs.	γ calc.	m	γ obs.	γ calc.
0.01	0.729	0.729	0.0053	0.932	0.925
0.02	0.662	0.664	0.01	0.901	0.901
0.05	0.571	0.575	0.0202	0.862	0.869
0.07	0.540	0.543	0.0526	0.805	0.813
0.1	0.512	0.512	0.1081	0.757	0.764
0.2	0.465	0.463	0.1934	0.732	0.730
0.5	0.427	0.431	0.3975	0.699	0.686
0.7	0.427	0.436	0.807	0.664	0.666
1.	0.449	0.454	1.020	0.666	0.670
			1.517	0.694	0.695
			2.024	0.728	0.734
			3.1	0.82	0.85

Electrolyte	A	B	$a \times 10^8$
HCl	0.940	0.0713	4.05
NaCl	0.840	0.0320	3.62
$SrCl_2$	1.018	0.03	4.39
NaOH	0.66	0.05	2.87

[1] Scatchard, *J. Am. Chem. Soc.*, **47**, 2098 (1925).
[2] Harned, *J. Am. Chem. Soc.*, **51**, 416 (1929).
[3] Harned, *J. Am. Chem. Soc.*, **48**, 326 (1926).
[4] Harned, and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

By measuring the electromotive forces of cells of the types

$$H_2(1\text{ atm.})\,|\,HX(m_0)\,|\,AgX\,|\,Ag,$$

and

$$H_2(1\text{ atm.})\,|\,HX(m_1), \qquad MCl_n(m_2)\,|\,AgX\,|\,Ag,$$

and their temperature coefficients, it is possible to compute the partial molal free energy, the partial molal heat content, and the activity coefficient of a halide acid in the halide solution. The cell reaction of the first cell is

$$\tfrac{1}{2}H_2(1\text{ atm.}) + AgX = Ag + HX(m_0),$$

and of the second

$$\tfrac{1}{2}H_2(1\text{ atm.}) + AgX = Ag + HX(m_1)[MX_n(m_2)],$$

since the halide acid is produced in a solution of halide acid (m_1) containing the halide at a concentration (m_2). By subtracting the second equation from the first, we obtain

$$HX(m_1)[MX_n(m_2)] = HX(m_0),$$

which represents the transfer of a mol of halide acid from the mixture to the solution containing halide acid only. This reaction will correspond to the double cell

$$Ag\,|\,AgX\,|\,HX(m_1), \qquad MX_n(m_2)\,|\,H_2\,|\,HX(m_0)\,|\,AgX\,|\,Ag,$$

from the electromotive force of which the partial molal free energy of the halide acid in the salt solution relative to its partial molal free energy in halide acid at a concentration m_0 may be readily computed by equation (7). If the temperature coefficient of the electromotive force is known, then the partial molal heat content of the acid in the mixture relative to its value in the pure acid may be calculated by equation (18) or (19).

The decrease in free energy, $(-\Delta\overline{F})$, equals the difference in partial molal free energies of the acid in the pure acid solution and the salt solution, and, therefore, according to equation (49),

$$(-\Delta\overline{F}) = -(\overline{F}_2 - \overline{F}_{2(s)}) = RTln\frac{a_{H(s)}a_{X(m_1+m_2)}}{a_{H(m_0)}a_{X(m_0)}}, \tag{161}$$

where $a_{H(s)}$ is the activity of the hydrogen ion in the salt solution. Consequently, if the activity product, $a_{H(m_0)}a_{X(m_0)}$ of the pure acid at a concentration m_0 is known, the activity product of the hydrogen and halide ions in the mixtures may be calculated. If we now substitute **NEF** for $(-\Delta\overline{F})$ and the activity coefficient concentration products for the activities, we readily obtain at 25°

$$\mathbf{E}_1 = 0.05915\log\frac{\gamma_{H(s)}\gamma_{X(s)}m_1(m_1+m_2)}{\gamma_{H(m_0)}\gamma_{X(m_0)}m_0^2}. \tag{162}$$

Similarly, the electromotive force of the cells

$$H_2\,|\,MOH(m_1), \qquad MX(m_2)\,|\,M_xHg\,|\,MOH(m_0)\,|\,H_2$$

are related to the activity coefficients of the metal and hydroxyl ions and the activities of the water molecules by the equation

$$\mathbf{E}_2 = 0.05915 \log \frac{\gamma_{M(s)}\gamma_{OH(s)}a_{H_2O(m_0)}m_1(m_1 + m_2)}{\gamma_{M(m_0)}\gamma_{OH(m_0)}a_{H_2O(s)}m_0^2}, \qquad (163)$$

where the subscript (s) as before refers to the salt solution. As an illustration of the application of this method to a unibivalent electrolyte, we may take the cells,

$$Hg\,|\,Hg_2SO_4\,|\,H_2SO_4(m_1), \qquad M_nSO_4(m_2)\,|\,H_2\,|\,H_2SO_4(m_0)\,|\,Hg_2SO_4\,|\,Hg.$$

In this case, the electromotive force and activity coefficient are related by the equation,

$$\mathbf{E} = \frac{0.05915}{2} \log \frac{\gamma_{H(s)}^2\gamma_{SO_4(s)}(2m_1)^2(m_1 + m_2)}{\gamma_{H(m_0)}^2\gamma_{SO_4(m_0)}(2m_0)^2m_0} \qquad (164)$$

$$= 0.08873 \log \frac{\gamma_{(s)}\sqrt[3]{m_1^2(m_1 + m_2)}}{\gamma \qquad m_0}. \qquad (164a)$$

Extensive studies of cells of these types have been made[1] from which the activity coefficients of the acids and hydroxides have been computed. A graphical representation of values obtained from these measurements in the case of constant 0.01 or 0.005 molal acids or hydroxides in the salt solutions

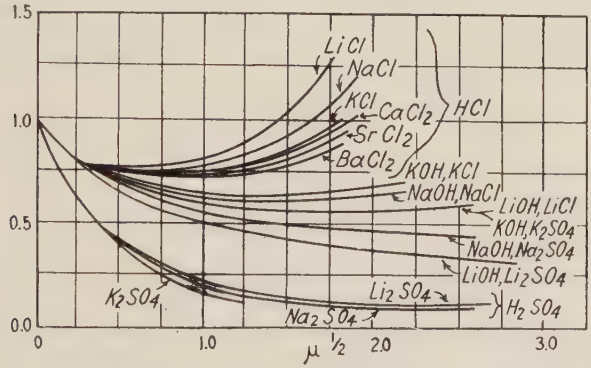

FIG. 16. Activity Coefficients of Hydrochloric, Sulphuric Acid, and Alkali Hydroxides in Homoionic Salt Solutions

is given in Fig. 16. The reference values in the pure hydroxide or acid solutions at m_0 concentration were obtained from Tables VIII and IX.

[1] Harned, *J. Am. Chem. Soc.*, **38**, 1986 (1916); **42**, 1808 (1920); **47**, 684 (1925); **47**, 689 (1925); **48**, 326 (1926); *Z. physik. Chem.*, **117**, 1 (1926); Harned and Brumbaugh, *J. Am. Chem. Soc.*, **44**, 2729 (1922); Harned and Sturgis, *J. Am. Chem. Soc.*, **47**, 945 (1925); Harned and Swindells, *J. Am. Chem. Soc.*, **48**, 126 (1926); Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926); Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926); Åkerlöf, *J. Am. Chem. Soc.*, **48**, 1160 (1926); Randall and Langford, *J. Am. Chem. Soc.*, **49**, 1445 (1927); Randall and Breckenridge, *J. Am. Chem. Soc.*, **49**, 1435 (1927).

We shall first discuss the properties common to all these results, and then contrast the behavior of the acid-salt systems with that of the hydroxide-salt systems.

The activity coefficients of these electrolytes in the salt solution behave similarly to those of simple strong electrolytes in the pure solvent, a fact which becomes apparent by comparison of these results with the data represented in Figs. 6, 7, and 8. This is in accord with theory since we find that the activity coefficient of an electrolyte in the mixtures will be a function of Γ or μ which quantities by definition depend on all the ions in the solution.[1]

The equation which results from Hückel's theory,

$$\log \gamma = -\frac{0.356 z_1 z_2 \sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} + B\Gamma_1 + B'(\Gamma - \Gamma_1) - \log\left(1 + \frac{M_0}{1000}\nu m_T\right) \quad (165)$$

obtained by adding the term $B'(\Gamma - \Gamma_1)$ to equation (159) may be employed to calculate γ for all these solutions. B' is a constant and is different for each salt solution in which the electrolyte whose activity coefficient is γ and whose Γ strength is Γ_1. An equation of similar form obtained by adding the term $\alpha''(\mu - m_1)$ to equation (158) has also been employed by Harned and Brumbaugh [2] for the same purpose.

We may summarize the specific behaviors of the activity coefficients of strong acids in the salt solutions by the following statement. At a given acid and total concentration, the activity coefficient of a strong acid is greater in the solution of the salt of a given valence type which in the pure solvent possesses the higher activity coefficient. This is just the opposite to the behavior of the strong hydroxides in the same salt solutions. Thus, we find that

$$\gamma_{KOH(KCl)} > \gamma_{NaOH(NaCl)} > \gamma_{LiOH(LiCl)},$$

and

$$\gamma_{KOH(KCl)} > \gamma_{KOH(KBr)} > \gamma_{KOH(KI)},$$

while

$$\gamma_{LiCl} > \gamma_{NaCl} > \gamma_{KCl},$$

and

$$\gamma_{KI} > \gamma_{KBr} > \gamma_{KCl}.^{3}$$

This behavior conforms with that of the hydroxides in the pure aqueous solutions which, as we have previously shown, is opposite to that of the halides.

It has been found possible by the use of Hückel's more general equations to calculate the activity coefficient of hydrochloric acid in halide solutions from the data on these electrolytes in pure aqueous solutions, and vice versa.[4] This is not necessarily a proof of Hückel's theory but confirms the formal validity of the method. The activity coefficients of the hydroxides in salt solutions,

[1] Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

[2] Harned and Brumbaugh, *J. Am. Chem. Soc.*, **44**, 2729 (1922).

[3] Harned and James, *J. Physical Chem.*, **30**, 1060 (1926).

[4] Hückel, *Physik. Z.*, **26**, 93 (1925); Harned, *J. Am. Chem. Soc.*, **48**, 326 (1926); Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

however, cannot be computed from the data on the individual electrolytes in the same manner. The results can be calculated by equation (165) if arbitrary values are assigned to A, B, and B'.

The Law of the Linear Variation of the Logarithm of the Activity Coefficient at Constant Total Molality: At constant total molality equation (165) reduces to

$$\log \gamma = (B - B')\Gamma_1 + \log \gamma_0, \tag{166}$$

where $\log \gamma_0$ is a constant and γ_0 is the activity coefficient of the electrolyte at zero concentration or zero Γ_1 in an electrolytic solution of strength Γ. For a uniunivalent electrolyte, this equation reduces to

$$\log \gamma = \alpha_1 m_1 + \log \gamma_0, \tag{167}$$

where α_1 equals $2(B - B')$. This latter expression, which states that the logarithm of the activity coefficient of a uniunivalent electrolyte in a solution of constant total molality containing another uniunivalent electrolyte varies linearly with its concentration, has been accurately tested for the case of hydrochloric acid in chloride solutions and found to be valid both in dilute and concentrated solutions. This has been shown by the extraordinarily accurate electromotive force measurements of Güntelberg.[1] He employed the cells

$$H_2 \,|\, HCl(0.1) \,|\, AgCl \,|\, Ag; \qquad \mathbf{E}_{0.1},$$

and

$$H_2 \,|\, HCl(m_1), \qquad MCl(m_2) \,|\, AgCl \,|\, Ag; \qquad \mathbf{E},$$

from which

$$\mathbf{E}_{0.1} - \mathbf{E} = \frac{RT}{\mathbf{N}\mathbf{F}} ln \frac{\gamma_H \gamma_{Cl} m_1 (m_1 + m_2)}{\gamma_{H(0.1)} \gamma_{Cl(0.1)} (0.1)^2}. \tag{168}$$

Let $\gamma_{HCl(0.1)}$ equal unity. Then

$$\mathbf{E} = \left[\mathbf{E}_{0.1} + \frac{2RT}{\mathbf{N}\mathbf{F}} ln\, 0.1 \right] - \frac{2RT}{\mathbf{N}\mathbf{F}} ln \gamma - \frac{RT}{\mathbf{N}\mathbf{F}} \left[ln m_1 + ln(m_1 + m_2) \right]. \tag{169}$$

At 20°, Güntelberg obtained 0.35324 for $\mathbf{E}_{0.1}$. Consequently,

$$\mathbf{E} = 0.23691 - 0.11633 \log \gamma - 0.058164 \left[\log m_1 + \log (m_1 + m_2) \right]. \tag{170}$$

From the observed values of $\mathbf{E}$, $(-0.11633 \log \gamma)$ may be computed, and since γ equals unity when the salt concentration is zero, the constant term, $\log \gamma_0$, in equation (167) is zero and

$$-0.11633 \log \gamma = \alpha x, \tag{171}$$

where $0.1\,x$ is the concentration of MCl. We give the values of $(-0.11633 \log \gamma)$ calculated by Güntelberg from the observed data in the second column in Table XIII. The third column contains the calculated values of αx, and

[1] Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

TABLE XIII

PROOF OF THE LAW OF THE LINEAR VARIATION OF LOG γ_{HCl} IN UNIUNIVALENT CHLORIDE SOLUTIONS

(1) CsCl

x	$-0.11633 \log \gamma$	$0.00170\ x$	Δ (m.v.)
0.5	0.00086	0.00085	−0.01
0.9	0.00153	0.00153	0.00

(2) KCl

x	$-0.11633 \log \gamma$	$0.00098\ x$	Δ (m.v.)
0.25	0.00026	0.00025	−0.01
0.5	0.00047	0.00049	0.02
0.7	0.00068	0.00068	0.01
0.9	0.00090	0.00090	−0.02

(3) NaCl

x	$-0.11633 \log \gamma$	$0.00049\ x$	Δ (m.v.)
0.3	0.00013	0.00015	0.02
0.6	0.00031	0.00029	−0.02
0.9	0.00044	0.00044	0.00

(4) LiCl

x	$-0.11633 \log \gamma$	$0.00008\ x$	Δ (m.v.)
0.3	0.00002	0.00002	0.00
0.6	0.00005	0.00005	0.00
0.9	0.00007	0.00007	0.00

the fourth the difference in millivolts between the observed and calculated values.

The agreement between the values of αx and $-0.11633 \log \gamma$ with a maximum deviation of only 0.02 *mv*, establishes this law at 0.1 total concentration to within 0.04 per cent. Harned,[1] by employing the less accurate calomel electrode obtained values for α of 0.0005 and 0.0010 for sodium and potassium chloride solutions which agree well with the values 0.00049 and 0.00098 obtained by Güntelberg.

That equation (167) is valid for the activity coefficients of hydrochloric acid in chloride solutions at high concentrations is made clear by Fig. 17. In

[1] Harned, *J. Am. Chem. Soc.*, **48**, 326 (1926).

this figure, the observed values of log γ are plotted against the molal concentration of the acid at a constant total molality of 3. The observed points are seen to lie on the straight lines. Indeed, more recent evidence shows that the law is valid for the hydrochloric acid sodium chloride mixtures at 6 M total molality.

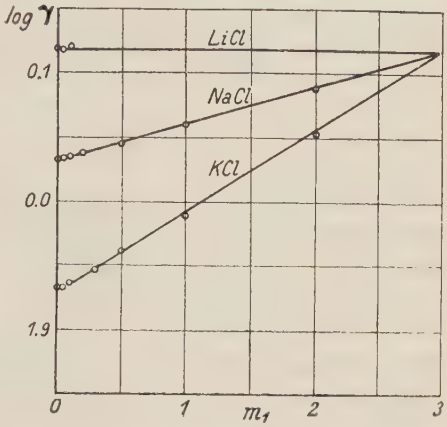

FIG. 17. The Linear Law of Variation of Log γ at 3M Constant Total Molality

Owing to the peculiarities of the thermodynamical properties of the hydroxides, hydroxide-salt mixtures show a departure from this law at high constant total molalities. Harned and Harris[1] have shown that only a very slight departure is observable in the case of potassium hydroxide-chloride mixtures at 3.5 M total concentrations. With sodium hydroxide-chloride mixtures, however, the plot of log γ of the hydroxide against the concentration of the hydroxide shows a distinct curvature at 3 M and a pronounced curvature at 5 M. At 3 M, the maximum deviation from the law was found to be 1.6 per cent, and at 5 M, 3.5 per cent.

It is a matter of considerable importance to extrapolate these results at constant molality to zero concentration of the electrolyte whose activity coefficient is under consideration. If we plot γ against log m as in Fig. 18, we observe that at concentrations below 0.01, γ varies very little with the concentration m. Indeed this variation is well within the usual experimental error.

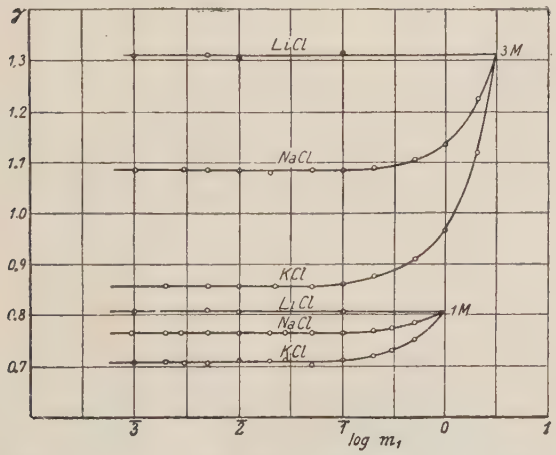

FIG. 18. γ — log m_1 Plot at Constant Total Molality

This is very valuable since it gives us a means of determining γ at zero acid concentration in a salt solution of any given molality. This extrapolation can likewise be made for systems, such as the hydroxide-salt systems which do not exactly conform to the law of the linear variation. We shall now proceed to consider a good example of the usefulness of this method of extrapolation.

[1] Harned and Harris, *J. Am. Chem. Soc.*, **50**, 2633 (1928).

The Ionic Activity Coefficient and Dissociation of Water in Salt Solutions: By extrapolating these results at constant total molality we are able to obtain at any salt concentration $\gamma_{H(0)}\gamma_X$ from measurements of the acid-halide cells, and $\frac{\gamma_M\gamma_{OH(0)}}{a_{H_2O}}$ at the same salt concentration from measurements of the hydroxide salt cells. Note that the hydrogen and hydroxyl ions are at zero concentration. If we multiply these two expressions we obtain $\frac{\gamma_{H(0)}\gamma_{OH(0)}}{a_{H_2O}}\gamma_M\gamma_X$. This quantity is known in the solution containing no acid or base but only salt. But, $\gamma_M\gamma_X$ is merely the square of the activity coefficient of the salt, and therefore, if we divide the above expression by this quantity we easily obtain $\frac{\gamma_{H(0)}\gamma_{OH(0)}}{a_{H_2O}}$. Since we have shown that at concentrations below 0.01 M acid or base, the values of γ are independent of the acid or base concentrations, $\frac{\gamma_{H(0)}\gamma_{OH(0)}}{a_{H_2O}}$ equals $\frac{\gamma_H\gamma_{OH}}{a_{H_2O}}$ where the latter quantity refers to the activity coefficient of water at hydrogen or hydroxyl ion concentrations of approximately 10^{-7}. Thus, without any assumption other than that these results at constant total molality may be extrapolated, it is possible to obtain the ionic activity coefficient of water in salt solutions.

The following scheme may be readily employed for the determination of $\frac{\gamma_H\gamma_{OH}}{a_{H_2O}}$ relative to its value at m_0 concentration from electromotive force data. Thus, if we let m_1 equal m_0 in equations (162) and (163), add these two equations and rearrange, we obtain

$$\mathbf{E}_1 + \mathbf{E}_2 = 0.05915 \log \frac{\gamma_{M(s)}\gamma_{X(s)}(m_2 + m_0)^2}{\gamma_{M(m_0)}\gamma_{X(m_0)}m_0^2} + 0.05915 \log \frac{\gamma_{H(s)}\gamma_{OH(s)}a_{H_2O(m_0)}}{\gamma_{H(m_0)}\gamma_{OH(m_0)}a_{H_2O(s)}}. \quad (172)$$

The first member on the right of this equation is the electromotive force of the cell

$$\mathrm{Ag}\,|\,\mathrm{AgX}\,|\,\mathrm{MX}(m_0 + m_2)\,|\,\mathrm{M}_x\mathrm{Hg}\,|\,\mathrm{MX}(m_0)\,|\,\mathrm{AgX}\,|\,\mathrm{Ag}; \qquad \mathbf{E}_3,$$

and obviously

$$\mathbf{E}_1 + \mathbf{E}_2 - \mathbf{E}_3 = 0.05915 \log \frac{\frac{\gamma_{H(s)}\gamma_{OH(s)}}{a_{H_2O(s)}}}{\frac{\gamma_{H(m_0)}\gamma_{OH(m_0)}}{a_{H_2O(m_0)}}} = 0.05915 \log \frac{K_{\gamma(s)}}{K_{\gamma(m_0)}}. \quad (173)$$

Thus, if $K_{\gamma(m_0)}$ is known, $K_{\gamma(s)}$ may be computed. This method is a very close approximation as long as m_0 is sufficiently low so as to fall on the portion of the curve in Fig. 18 which is parallel to the abscissa. That is to say, the

concentration, m_0, of the acid and hydroxide should be sufficiently low so that γ_{HX} or γ_{MOH} is independent of the concentration of the acid or base.

From the knowledge of $K_{\gamma(s)}$ obtained by these methods, it is now possible to calculate the dissociation of water in the salt solutions. The thermodynamic law of the equilibrium between water and the ions produced by its dissociation is

$$K = \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} m_H m_{OH} = K_{\gamma(s)} m_H m_{OH} \qquad (174)$$

and, therefore, since $K_{\gamma(s)}$ relative to its value at m_0 concentration may be determined, $m_H m_{OH}$ may be computed relative to m_0. Further if m_0 is small it may be evaluated by the equations of Debye and Hückel, and $K_{\gamma(s)}$ computed relative to unity at zero salt concentration. Then by taking the dissociation constant K equal to 10^{-14} at 25°, the absolute values of $m_H m_{OH}$ and therefrom m_H and m_{OH} in the salt solutions may be obtained.

Fig. 19 contains plots of $K_{\gamma(s)}$ against the square root of the ionic strength for some univalent halides. These were taken from the measurements of

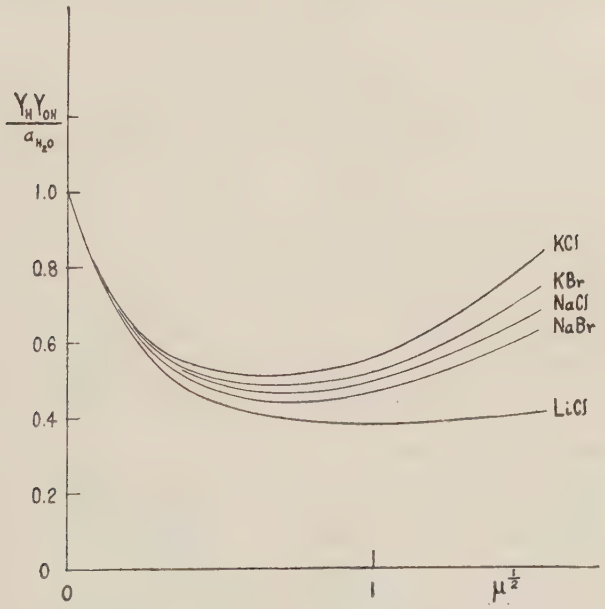

FIG. 19. The Ionic Activity Coefficient Product of Water in Halide Solutions

Harned, Harned and Swindells, and Harned and James.[1] The form of these curves follows those of activity coefficients in concentrated solutions and shows the characteristic minima. Further, the distribution follows the rule that the

[1] Harned, *J. Am. Chem. Soc.*, **47**, 930 (1925); Harned and Swindells, *ibid.*, **48**, 126 (1926); Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

values of the activity coefficient are less in a solution of a given strength in the solution containing the salt which possesses the higher activity coefficient.

In Fig. 20, the values of the hydrogen or hydroxyl ion concentrations of water in the salt solutions are shown. Upon first addition of salt the dissociation of water rapidly increases due to the rapid decrease in $K_{\gamma(s)}$. This

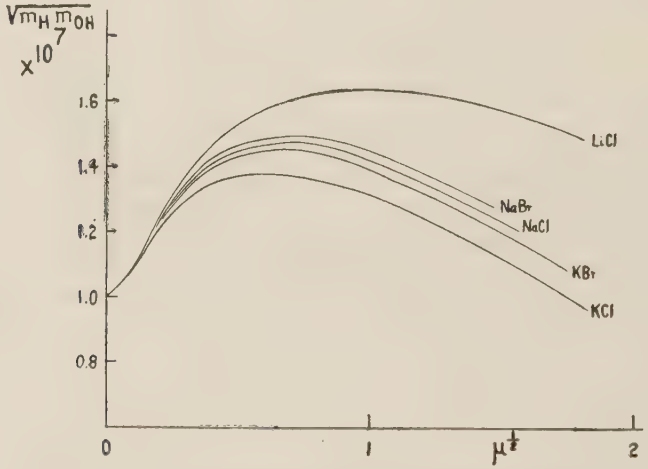

Fig. 20. The Ionic Dissociation of Water in Halide Solutions

phenomenon will also occur in the case of all weak electrolytes upon the first addition of salt. This was pointed out by Arrhenius from consideration of the increase in catalytic activity of acetic acid by the addition of potassium chloride. Brönsted [2] showed that such an increase in dissociation of a weak electrolyte was to be expected in the dilute solution because of the decrease in the activity coefficient. In the more concentrated solutions, maxima are obtained, and at concentrations higher than those corresponding to the maxima the dissociation decreases. The order of the results is of course the reverse of those of the activity coefficients.

The Ionization of Weak Electrolytes: As a further result of the action of the interionic forces and the presence of an ionic atmosphere, it is found that when an electrolytic solution is subjected to external forces as in the case of electrolytic conductance, the presence of the ionic atmosphere of an ion will cause a lag in the velocity with which it moves through the solution. Debye and Hückel,[2] and particularly, Onsager have investigated this question and have obtained from considerations of both the interionic and the superimposed forces a limiting law for the equivalent conductance, which seems to be very nearly valid in the cases of dilute solutions of strong electrolytes in aqueous solutions.

If we take into account the activity coefficients, the dissociation of a weak

[1] Brönsted, *J. Chem. Soc.*, **119**, 574 (1921).

[2] Debye and Hückel, *Physik. Z.*, **24**, 305 (1923); Onsager, *Physik Z.*, **28**, 277 (1927).

univalent electrolyte is given by the equation

$$K = \frac{\alpha\gamma_+ \alpha\gamma_- m}{(1-\alpha)\gamma}, \tag{175}$$

where α is the degree of dissociation, γ, γ_+, and γ_- are the activity coefficients of the undissociated molecule, the cation, and anion, respectively. In very dilute solutions γ may be taken to equal unity, and $\gamma_+\gamma_-$ will vary according to equation (147).

The question now arises as to how to obtain the degree of dissociation from conductance measurements when we take into consideration the effects of interionic attraction. According to the classical theory α is equal to Λ/Λ_0 where Λ_0 is the molecular conductance at zero ionic strength. We have shown previously that this can only be true if the mobilities do not change with the concentrations. The mobilities, however, are a function of the concentration or ionic strength according to the interionic attraction theory. To correct for this effect, Sherrill and Noyes, and MacInnes have employed the following simple calculation. Consider a solution of acetic acid at a dilute concentration m. Instead of computing α by

$$\Lambda = \alpha(U_c + U_a)\mathbf{F} = \alpha(\Lambda_c + \Lambda_a), \tag{176}$$

where Λ_c and Λ_a are the ionic conductances at infinite dilution, we determine $(\Lambda_c + \Lambda_a)$ at the ionic strength of the acetic acid from the molecular conductance of completely ionized electrolytes. In very dilute solutions, MacInnes [1] has shown that for many strong simple electrolytes the ionic conductances are additive. Thus,

$$\Lambda_{HCl} + \Lambda_{NaAc} - \Lambda_{NaCl} = \Lambda_{HAc} = \Lambda_c' + \Lambda_a',$$

which is the desired molecular conductance of completely dissociated acetic acid at the ionic strength of m molal acetic acid. By substituting this value in equation (176) the corrected values of α may be determined. This value of α, and the value of γ computed by the Debye-Hückel theory were substituted in equation (175), and very constant values for K were obtained in the dilute solutions. Sherrill and Noyes [2] have successfully applied this method to moderately ionized electrolytes, and MacInnes [3] has also obtained good results for cases of acetic and some substituted acetic and benzoic acids.

The Activity Coefficients and Dissociation of Weak Electrolytes in Salt Solutions: [4] We have shown how the ionic activity coefficient and dissociation of water may be determined in salt solutions. The method used may also be applied to determine the dissociation and ionic activity coefficients of other solvents, and likewise in a somewhat modified form for the determination of

[1] MacInnes, *J. Am. Chem. Soc.*, **41**, 1086 (1919); **43**, 1217 (1921).
[2] Sherrill and Noyes, *J. Am. Chem. Soc.*, **48**, 1861 (1926).
[3] MacInnes, *ibid.*, **48**, 2068 (1926).
[4] Harned and Robinson, *J. Am. Chem. Soc.*, **50**, 3157 (1928).

the ionic activity coefficients of weak acids and bases in salt solutions. We shall show that this result may be accomplished by the use of cells without liquid junction which contain easily reproducible electrodes such as the hydrogen and silver-silver chloride electrodes.

If the activity product, $a_c a_a$, of the ions of a weak uniunivalent electrolyte has been determined, we may define an activity coefficient by either

$$(1) \quad \gamma = \sqrt{\frac{a_c a_a}{m_c m_a}} \qquad \text{or} \qquad (2) \quad \gamma = \sqrt{\frac{a_c a_a}{m_+ m_-}}. \tag{177}$$

In (1) m_c and m_a are the stoichiometrical molalities of the ion groups of the electrolyte. Thus, in a solution of $HAc(m_1) + NaAc(m_2)$, m_c equals m_1 and m_a equals $(m_1 + m_2)$ and in a solution of $HAc(m_1) + NaCl(m_2)$, m_c equals m_a equals m_1. In (2), m_+ and m_- are the true molal concentrations of the ionic species. In the following discussion $\sqrt{\gamma_+\gamma_-}$ is the quantity defined by the second of these equations. Indeed, it is the more important since it is directly comparable to the activity coefficients of strong electrolytes.

Let us consider the cell:

$$\mathrm{Ag}\,|\,\mathrm{AgX}\,|\,\mathrm{HX}(m_0), \quad \mathrm{MX}(m_3)\,|\,\mathrm{H_2}\,|\,\mathrm{HAc}(m_1), \quad \mathrm{MX}(m_2)\,|\,\mathrm{AgX}\,|\,\mathrm{Ag}.$$

The cell reaction represents the transfer of HX from the solution containing the strong acid, HX, to the solution containing HAc. Its electromotive force, therefore, will be given by:

$$\mathbf{E} = 0.05915 \log \frac{\gamma_{H(2)}\gamma_{X(2)} m_0 (m_3 + m_0)^1}{\gamma_{H(1)}\gamma_{X(1)} m_H m_2}, \tag{178}$$

where $\gamma_{H(2)}\gamma_{X(2)}$ is the activity coefficient product of the ions in the solution containing HX and $\gamma_{H(1)}\gamma_{X(1)}$ the same in the solution containing HAc. m_H is the stoichiometrical molality of the hydrogen ion. Now, under certain conditions $\gamma_{H(2)}\gamma_{X(2)}$ may be taken to equal $\gamma_{H(1)}\gamma_{X(1)}$. Let us take the total ionic strengths of the two solutions in the cell equal, that is to say that $m_3 + m_0 = m_H + m_2$. In the first place, we have found that in solutions of constant total molality containing acids at concentrations of 0.01 M or lower, $\gamma_H\gamma_X$ may be regarded as independent of the acid concentration (see Fig. 18). Therefore, $\gamma_{H(2)}\gamma_{X(2)}$ equals $\gamma_{H(1)}\gamma_{X(1)}$ provided that the concentration of the undissociated molecule, Hac, is sufficiently low (less than 0.2 M) so as not to influence appreciably the magnitude of $\gamma_{H(2)}\gamma_{X(2)}$. With these provisos, equation (178) reduces to

$$\mathbf{E} = 0.05915 \log \frac{m_0 (m_3 + m_0)}{m_H m_2}, \tag{179}$$

and since m_0, m_2, and m_3 are known, m_H may be evaluated. We shall not consider what may be expected to happen when HAc is present at high concentrations although this point is discussed by Harned and Robinson.

[1] See equation (162).

After having computed m_H by equation (179), the calculation of $\frac{\gamma_H\gamma_{Ac}}{\gamma_{HAc}}$ can be accomplished by means of the thermodynamic equation for the dissociation of the acid, namely:

$$K = \frac{\gamma_H\gamma_{Ac}}{\gamma_{HAc}} \frac{m_H^2}{m_1 - m_H} . \tag{180}$$

Since K, m_1, and m_H are now known, the ionic activity coefficient product, $\frac{\gamma_H\gamma_{Ac}}{\gamma_{HAc}}$, which we denote γ_A, and which corresponds to the quantity $\frac{\gamma_H\gamma_{OH}}{a_{H_2O}}$ previously determined, may readily be computed.

Exactly similar considerations when applied to cells of the type:

$$H_2 | MOH(m_0), \quad MX(m_3) | M_XHg | BOH(m_1), \quad MX(m_2) | H_2,$$

in which MOH is a strong and BOH a weak hydroxide, will lead to an equation similar to equation (179), by means of which the hydroxide ion concentration in the salt solution containing the weak base may be calculated. From these values, by means of the equation corresponding to (179) and applied to the weak base, the ionic activity coefficient product, $\frac{\gamma_B\gamma_{OH}}{\gamma_{BOH}}$ which we denote γ_R may be obtained.

In Figs. 21 and 22 we have plotted some values of $\sqrt{\gamma_A}$ and $\sqrt{\gamma_R}$ which have been obtained from the data of Harned and Robinson.[1] Fig. 21 contains

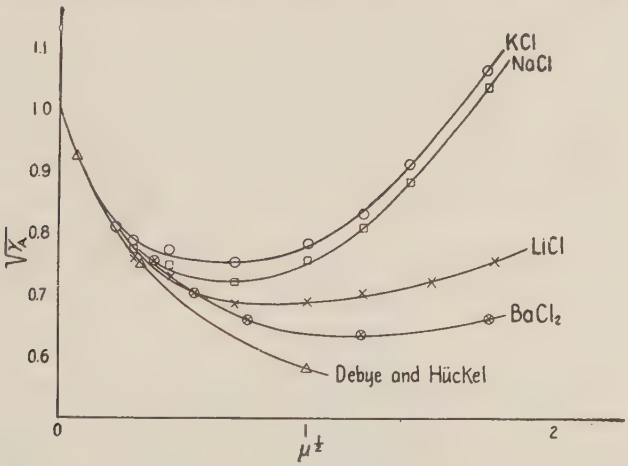

FIG. 21. The Ionic Activity Coefficient of Acetic Acid in Salt Solutions

the value γ_A of the ionic activity coefficient of acetic acid in potassium, sodium, lithium, and barium chloride solutions. These curves are observed to possess

[1] Harned and Robinson, *J. Am. Chem. Soc.*, **50**, 3157 (1928).

properties which include the characteristic minima like those of the strong electrolytes, (Figs. 6, 7, 8, 16). They agree in the dilute solutions with values computed by equation (156) of the Debye and Hückel theory if A is assigned a probable value of 0.8. This is shown by Fig. 21. Further, at a given concentration the order of the curves is the same as that of the ion activity coefficient product of water and of strong hydroxides in salt solutions. Since this is the case the curves for the dissociation of acetic acid in the salt solutions will have the characteristics of the results plotted in Fig. 20.

Fig. 22 contains the values of $\sqrt{\frac{\gamma_B \gamma_{OH}}{\gamma_{BOH}}}$ or $\sqrt{\gamma_R}$ for ammonia, and moni-, di, and trimethylamines in sodium chlroide solutions, which were computed by a similar method. The effect of substitution of the ammonia molecule by methyl groups is seen to lower $\sqrt{\gamma_R}$ at a given salt concentration.

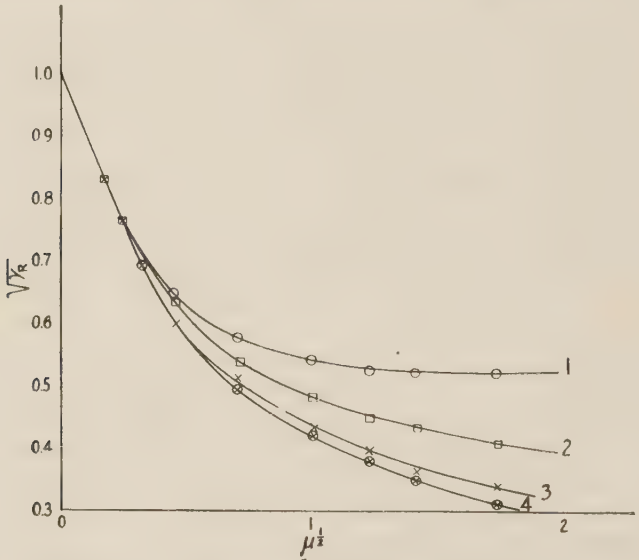

Fig. 22. The Ionic Activity Coefficient of Weak Bases in Sodium Chloride Solutions
1 Ammonia
2 Monomethylamine
3 Dimethylamine
4 Trimethylamine

This method leads to a wide field of investigation, since we shall be able to study the effects of the powerful electric fields of electrolytic solutions upon the characteristic potentials produced by the presence of organic ions.

Cells with Liquid Junctions. Calculation of Transference Numbers. Liquid Junction Potentials

The cell without liquid junction is the only type which has yet been considered, and it has been shown that from measurements of such cells activity

products and mean activity coefficients may be computed with exactness. We have yet to consider cells with liquid junctions.

The electromotive force, **E**, of the cell

$$\mathrm{Li}_x\mathrm{Hg}\,|\,\mathrm{LiCl}(m')\,|\,\mathrm{LiCl}(m'')\,|\,\mathrm{Li}_x\mathrm{Hg},$$

where m'' is greater than an m', is equal to the sum of the two electrode potentials, and the potential at the boundary of the two solutions. This electromotive force may be expressed by

$$\mathbf{E} = \frac{RT}{\mathbf{F}} ln \frac{a''}{a'} + \mathbf{E}_1, \tag{181}$$

where a' and a'' are the activities of the lithium ion at concentrations m' and m'', respectively, and $\mathbf{E}_1$ is the liquid junction potential. However, it is important to note that the value of $\mathbf{E}_1$ depends on the activity ratio of the ions and since individual ionic activities have not been defined, $\mathbf{E}_1$ cannot be evaluated. We are thus confronted with the interesting perplexity that it is not possible to compute liquid junction potentials without a knowledge of individual ion activities, and it is not possible to determine individual ion activities without an exact knowledge of liquid junction potentials. We shall now proceed to show that no possible measurements of cells with or without transference can give any information regarding the individual ion activities or the magnitudes of the liquid junction potentials.

Concentration Cells with Liquid Junctions: The general formula for the electromotive force of a concentration cell with transference may be obtained in the following simple manner as has been shown recently by Taylor.[1] Consider the cell,

$$\text{Electrode (1)}\ \left|\begin{matrix} m_1, m_2, \cdots m_i, \cdots m_s \\ m_1', m_2', \cdots m_i', \cdots m_s' \end{matrix}\right|\ \text{Electrode (1)},$$

in which electrode (1) is reversible to ion (1) at concentrations m_1 and m_1' on the two sides of the cell. The "ms" and "$m's$" are the concentrations of the ions, odd subscripts refer to cations, even to anions. The electromotive force of this cell, $d\mathbf{E}_{1(\tau)}$ is given by

$$d\mathbf{E}_{1(\tau)} = \frac{d\bar{F}_1}{\mathbf{N}_1\mathbf{F}} - \frac{t_1 d\bar{F}_1}{\mathbf{N}_1\mathbf{F}} + \frac{t_2 d\bar{F}_2}{\mathbf{N}_2\mathbf{F}} - \frac{t_3 d\bar{F}_3}{\mathbf{N}_3\mathbf{F}} + \cdots, \tag{182}$$

where the "t_is" are the transference numbers of the ionic species and where $\sum_1^s \frac{t_i d\bar{F}_i}{\mathbf{N}_i\mathbf{F}}$ corresponds to the liquid junction potential $\mathbf{E}_1$ in equation (181). The term $\sum_1^s t_i d\bar{F}_i$ represents the sum of the free energy changes of all the ions at the boundary. If we place between the two solutions an electrode reversible to anion (2), we obtain the cell without transference

$$\text{Electrode (1)}\ \left|\begin{matrix} m_1, m_2, \cdots m_i, \cdots m_s \\ \text{(2)}\ \ m_1', m_2', \cdots m_i', \cdots m_s' \end{matrix}\right|\ \text{Electrode (1)},$$

[1] P. B. Taylor, *J. Phys. Chem.*, **31**, 1478 (1927).

whose electromotive force is given by

$$d\mathbf{E}_{12} = \frac{d\bar{F}_1}{\mathbf{N}_1\mathbf{F}} + \frac{d\bar{F}_2}{\mathbf{N}_2\mathbf{F}}, \qquad \text{or} \qquad \frac{d\bar{F}_2}{\mathbf{N}_2\mathbf{F}} = -\frac{d\bar{F}_1}{\mathbf{N}_1\mathbf{F}} + d\mathbf{E}_{12}. \tag{183}$$

Further, the cell obtained by replacing (2) by an electrode (3) reversible to cation 3 will possess an electromotive force, dE_{13} which is given by

$$d\mathbf{E}_{13} = \frac{d\bar{F}_1}{\mathbf{N}_1\mathbf{F}} - \frac{d\bar{F}_3}{\mathbf{N}_3\mathbf{F}}, \qquad \text{or} \qquad \frac{d\bar{F}_3}{\mathbf{N}_3\mathbf{F}} = +\frac{d\bar{F}_1}{\mathbf{N}_1\mathbf{F}} - d\mathbf{E}_{13}. \tag{184}$$

Similar equations may be obtained for the other cations.

By substituting these values in equation (182), we obtain

$$d\mathbf{E}_{1(\tau)} = \frac{d\bar{F}_1}{\mathbf{N}_1\mathbf{F}} - \frac{t_1 d\bar{F}_1}{\mathbf{N}_1\mathbf{F}} - \frac{t_2 d\bar{F}_1}{\mathbf{N}_1\mathbf{F}} + t_2 d\mathbf{E}_{12} - \frac{t_3 d\bar{F}_1}{\mathbf{N}_1\mathbf{F}} + t_3 d\mathbf{E}_{13} - \cdots \tag{185}$$

or

$$d\mathbf{E}_{1(\tau)} = \frac{d\bar{F}_1}{\mathbf{N}_1\mathbf{F}} - (t_1 + t_2 + \cdots + t_i \cdots + t_s)\frac{d\bar{F}_1}{\mathbf{N}_1\mathbf{F}} + t_2 d\mathbf{E}_{12} + t_3 d\mathbf{E}_{13} + \cdots. \tag{186}$$

Since the sum of the transference numbers equals unity, we easily find that

$$d\mathbf{E}_{1(\tau)} = t_2 d\mathbf{E}_{12} + t_3 d\mathbf{E}_{13} + \cdots. \tag{187}$$

A similar formula may be obtained when the ion transferred is an anion if the cation and anion subscripts be permuted. This equation may be integrated in the case of a cell in which the concentrations vary continuously across the boundary through a finite range. We thus obtain

$$\mathbf{E}_{1(\tau)} = \int t_2 d\mathbf{E}_{12} + \int t_3 d\mathbf{E}_{13} + \cdots \tag{188}$$

as the general formula for the cell with transference.

It is important that in this deduction the ionic free energies, $d\bar{F}_i$, are eliminated, and, consequently, the electromotive force of the cells are expressed in terms of the sums of the free energies of positive and negative ions which may be regarded as molecular free energies. Turning now to equation (182), it is to be observed that if the transference number of an ion, t_i, is a function of the ionic energy, $\bar{F}_i$, only, then it might be possible to obtain ionic free energies from measurements of cells with transference. But in fact we now know that this is not the case but that the mobility and transference numbers of the ions are influenced by their ionic atmospheres and are therefore functions of the properties of all the ions in the solution. This latter point is very simply proved in Taylor's discussion of this subject. *We are therefore forced to the conclusion that measurements of the electromotive forces of cells with transference*

can yield no information regarding ionic free energies and, consequently ionic activities.

In deriving equations (187) and (188), we have neglected the possible effect of the transfer of solvent. This can take place at the electrode by hydration and can also be effected at the boundary by the ion carriers. If s_0 is the quantity transferred by the electrode processes, and s_i that quantity carried across the boundary by the ith ion, then it can be shown that

$$\mathbf{E}_{1(\tau)} = \int t_2 d\mathbf{E}_{12} + \int t_3 d\mathbf{E}_{13} + \cdots \pm \int s_0 d\bar{F}_s + \sum_1^s \int s_i d\bar{F}_s \qquad (189)$$

where $d\bar{F}_s$ is the differential of the free energy of the solvent on passing from one solution to the other.

The Determination of Transference Numbers from Electromotive Force Data: Equation (187) is the one usually employed for the determination of transference numbers from electromotive forces of cells with and without liquid junctions. If both sides of this equation be integrated between two concentration limits, m_1 to m_2, we obviously obtain for the case of cells containing one electrolyte,

$$\mathbf{E}_{1(\tau)} = \int_{m_1}^{m_2} d\mathbf{E}_{1(\tau)} - \int_{m_1}^{m_2} t_1 d\mathbf{E}_{12} = t_1 \mathbf{E}_{12}, \qquad (190)$$

where t_1 is now the mean transference number between the two concentrations in question.[1] However, since the transference numbers of most ions vary considerably with change of concentration, it is more desirable to obtain this quantity at a given concentration. To accomplish this, we may use equation (187) which for a single electrolyte becomes

$$d\mathbf{E}_\tau = t_c d\mathbf{E}_{12} \qquad (191)$$

in the case where the electrodes of the cell with transference are reversible with respect to the anion. t_c is the cation transference number. If $\mathbf{E}_t$ be plotted against corresponding values of $\mathbf{E}_{12}$, of concentration cells of which one concentration is fixed and the other varied, the slope of the curve obtained will be the cation transference number. By employing a similar procedure which involved the method of least squares, MacInnes and Beattie [2] determined the transference numbers of the lithium ion from measurements of the cells

$$\mathrm{Ag}\,|\,\mathrm{AgCl}\,|\,\mathrm{LiCl}(m_1)\,|\,\mathrm{LiCl}(m_2)\,|\,\mathrm{AgCl}\,|\,\mathrm{Ag},$$

and

$$\mathrm{Ag}\,|\,\mathrm{AgCl}\,|\,\mathrm{LiCl}(m_1)\,|\,\mathrm{Li}_x\mathrm{Hg}\,|\,\mathrm{LiCl}(m_2)\,|\,\mathrm{AgCl}\,|\,\mathrm{Ag}.$$

In Table XIV are given their values, which are compared with values obtained by the Hittorf method.

[1] First suggested by Helmholtz, *Wied. Ann.*, **3**, 201 (1878); *Ber.*, **7**, 27 (1882); Ges. Abhl., **1**, 840; **2**, 979.

[2] MacInnes and Beattie, *J. Am. Chem. Soc.*, **42**, 1117 (1920).

TABLE XIV

TRANSFERENCE NUMBERS OF THE LITHIUM ION IN SOLUTIONS OF LITHIUM CHLORIDE

m	n_e (E.M.F.)	n_0 (Hittorf)
0.001	0.359	—
0.005	0.341	—
0.01	0.334	0.332
0.02	0.327	0.328
0.05	0.318	0.320
0.1	0.311	0.313
0.2	0.304	0.304
0.3	0.299	0.299
0.5	0.293	—
1	0.286	—
2	0.276	—
3	0.268	—

The agreement is striking. This method has been used with considerable success in a number of investigations.[1]

Consideration of and Equations for Liquid Junction Potentials: If we compare equations (181) and (182), we find that the liquid junction potential, $\mathbf{E}_1$, is given in general by the expression

$$\mathbf{E}_1 = -\sum_1^s \int_1^2 \frac{t_i d\bar{F}_i}{\mathbf{N}_i \mathbf{F}}, \tag{192}$$

where the integration is to be taken from solution (1) to solution (2) and the summation is for all the ions. If we substitute $RTdlna_i$ for $d\bar{F}_i$, we obtain

$$\mathbf{E}_1 = -\sum_1^s \frac{RT}{\mathbf{N}_i \mathbf{F}} \int_1^2 t_i dlna_i, \tag{193}$$

which is true as long as there is no solvent transfer. For the sake of simplification we shall consider only univalent ions. By introducing for a_i its equivalent, $\gamma_i m_i$, we may split up this equation into two parts as follows

$$\mathbf{E}_1 = -\sum_1^s 0.05915 \int_1^2 t_i d \log m_i - \sum_1^s 0.05915 \int_1^2 t_i d \log \gamma_i.^2 \tag{194}$$

The first integral is the one with which the classical theory dealt, and the second integral gives the deviation from the classical theory which is caused by the action of the interionic forces. Liquid junction potentials in the ideal region of concentration may now be defined by the use of usual convention

[1] MacInnes and Parker, *J. Am. Chem. Soc.*, **37**, 1445 (1915); Pearce and Hart, *J. Am. Chem. Soc.*, **43**, 2483 (1921); Knobel, *J. Am. Chem. Soc.*, **45**, 70 (1923); Harned and Fleysher, *J. Am. Chem. Soc.*, **47**, 92 (1925); Lucasse, *Z. physik. Chem.*, **121**, 254 (1926); *J. Phys. Chem.* **30**, 562 (1926).

[2] Harned, *J. Phys. Chem.*, **30**, 433 (1926).

that at infinite dilution all the "γ_is" equal unity. Equation (194) then becomes

$$\mathbf{E}_1 = -\sum_1^s 0.05915 \int_1^2 t_i d \log m_i. \tag{195}$$

On the basis of the classical theory, Planck [1] deduced a general equation for any kind of liquid junction. One feature of Planck's deduction was that he assumed an initially sharp boundary between the solutions, as a result of which the mixing could only take place by diffusion. More recently, Henderson,[2] obtained a solution of equation (195) upon the assumption of an initial mixing at the boundary. The Henderson equation for this reason gives for most types of boundaries values somewhat different from the Planck equation.

In order to illustration the method of evaluating the integral of equation (195), we shall employ the method of Henderson and indicate how his equation was obtained. We consider the boundary

$$\begin{array}{cc} \text{Solution (1)} & \text{Solution (2)} \\ \left| m_1, m_2, \cdots m_i, \cdots m_s \right| & m_1', m_2', \cdots m_i', \cdots m_s' \end{array} \Big|,$$

where the odd subscripts are univalent cations and the even univalent anions. We shall assume that where the two solutions meet, there will be a layer in which the concentrations vary uniformily from pure solution (1) to pure solution (2). Imagine a plane in this layer at which the fraction of solution (1) mixed with solution (2) is x, and, therefore, the fraction of solution (2) mixed with solution (1) is $(1 - x)$. At this plane the concentration of the ith species in solution (1) will be $m_i x$ and therefore $dm_i = m_i dx$. The part of the liquid junction potential due to the ions in solution (1) will according to equation (195) be expressed by

$$\mathbf{E}_{1(1)} = -\sum_1^s 0.05915 \int_0^1 t_i \frac{dx}{x}. \tag{196}$$

Similarly the concentration of the ith ion in solution (2) will be $m_i(1 - x)$ and $dm_i = -m_i' dx$ whence the contribution to the liquid junction potential of the ions in solution (2) will be

$$\mathbf{E}_{1(2)} = +\sum_1^s 0.05915 \int_0^1 t_i' \frac{dx}{(1 - x)}, \tag{197}$$

and, consequently, the total liquid junction will be given by

$$\mathbf{E}_1 = -\sum_1^s 0.05915 \int_0^1 t_i \frac{dx}{x} + \sum_1^s 0.05915 \int_0^1 t_i' \frac{dx}{(1 - x)}. \tag{198}$$

[1] Planck, *Wied. Ann.*, **39**, 161 (1890); **40**, 561 (1890).

[2] Henderson, *Z. physik. Chem.*, **59**, 118 (1907); **63**, 325 (1908).

The transference number of the i^{th} ion will be given by

$$t_i = \frac{u_i m_i x}{\sum_1^s u_i m_i x + \sum_1^s u_i' m_i' (1 - x)} \tag{199}$$

and a similar expression may be written for t_i'. The "$u_i s$" and "$u_i' s$" are the mobilities. If this expression be substituted for the transference numbers in (198) and the integration performed with the condition that the mobilities do not change with the concentration, we obtain Henderson's formula which is

$$\mathbf{E}_1 = 0.05915 \frac{(U_1 - V_1) - (U_2 - V_2)}{(U_1' - V_1') + (U_2' - V_2')} \log \frac{(U_1' + V_1')}{(U_2' + V_2')},^1 \tag{200}$$

where the quantities U_1, V_1, U_1', and V_1' are defined by

$$\left.\begin{aligned} U_1' &= u_1 m_1 + u_3 m_3 + u_5 m_5 + \cdots, \\ V_1' &= u_2 m_2 + u_4 m_4 + u_6 m_6 + \cdots, \\ U_2' &= u_1' m_1' + u_3' m_3' + u_5' m_5' + \cdots, \\ V_2' &= u_2' m_2' + u_4' m_4' + u_6' m_6' + \cdots. \end{aligned}\right\} \tag{201}$$

If we now consider the application of this equation to a simple junction as for example

$$\mathrm{MX}(m') \,|\, \mathrm{MX}(m''),$$

we obtain

$$\mathbf{E}_1 = 0.05915 \, (t_{\mathrm{M}} - t_{\mathrm{X}}) \log \frac{m'}{m''}. \tag{202}$$

This equation which was first obtained by Nernst [2] is thus shown to be valid as a limiting law in the very dilute solutions. The application of equation (200) to the junction

$$M_1\mathrm{X}(m) \,|\, \mathrm{M_2X}(m)$$

gives us

$$\mathbf{E}_1 = 0.05915 \log \frac{U_{\mathrm{M_1}} + U_{\mathrm{X}}}{U_{\mathrm{M_2}} + U_{\mathrm{X}}}. \tag{203}$$

Lewis and Sargent [3] modified this equation by substituting the molecular conductance ratio for the ratio of the sums of the mobilities. Such a procedure probably diminishes the error caused by the change in mobilities with

[1] By using the more general equation (192) and introducing some approximate relations to take into account the variation of the ionic conductances and activity coefficients with the concentration, Taylor has obtained (P. D. Taylor, *J. Phys. Chem.*, **31**, 1478 (1927)) an equation similar in form but of a more general type than Henderson's.

[2] Nernst, *Z. physik. Chem.*, **4**, 129 (1889).

[3] Lewis and Sargent, *J. Am. Chem. Soc.*, **31**, 363 (1909).

a change in concentration. They accordingly obtained for uniunivalent electrolytes

$$E_1 = \pm 0.05915 \log \frac{\Lambda_1}{\Lambda_2}. \qquad (204)$$

The liquid junction potential is positive when anion, negative when cation is common. A simple deduction of Lewis and Sargent's formula which illustrates the kind of reasoning and the assumptions necessary has been made by MacInnes and Yeh.[1] They show that it follows from the arbitrary assumption that the activity of the common ion is the same in both solutions.

Many difficulties are encountered in the measurements of liquid junction potentials. In the first place, the values observed by different investigators differ, because of the different methods employed in establishing the liquid junctions. Little difficulty has been encountered in reproducing the electromotive forces of cells in which the liquid junction is between two solutions of the same electrolyte at different concentrations. The situation is quite otherwise with many cells in which the liquid junction is found between solutions of different electrolytes. A careful investigation of the methods of establishing liquid junctions was made by Lewis, Brighton and Sebastian.[2] They finally employed a method whereby the two solutions were joined by dipping a tube containing one solution into a wider tube containing the other solution, and observed that, although the liquid junction potentials varied during the first few seconds, they soon reached a constant value, Lamb and Larson[3] have shown that many factors affect liquid junction potential measurements, and have found that a junction formed by two flowing solutions gave much more reproducible results than any other kind of junction yet investigated. The flowing junction may have a potential somewhat different from the stationary junction. The magnitude of this difference and the applicability of Lewis and Sargent's formula are illustrated in Table XV in which are included some measurements by MacInnes and Yeh[4] and Lewis, Brighton, and Sebastian[2] on cells of the type

$$\mathrm{Ag}\,|\,\mathrm{AgCl}\,|\,\mathrm{MCl}(m)\,|\,\mathrm{M'Cl}(m)\,|\,\mathrm{AgCl}\,|\,\mathrm{Ag},$$

where M and M′ are univalent cations. If we assume that the activities of the chloride ion are the same in the two solutions, it is clear that the total electromotive force of the cell is equal to the liquid junction potential. MacInnes and Yeh (M. and Y.) employed the flowing junction method, while the observations of Lewis, Brighton and Sebastian (L., B., and S.) were made on stationary junctions. In the last column are given the values computed by Lewis and Sargent's formula.

[1] MacInnes and Yeh, *J. Am. Chem. Soc.*, **43**, 2563 (1921); Taylor, Treatise on Physical Chemistry, 1st Edition, Vol. II, Chap. XII, p. 786 et seq. Van Nostrand & Co., New York, 1924.

[2] *J. Am. Chem. Soc.*, **39**, 2245 (1917).

[3] *J. Am. Chem. Soc.*, **42**, 229 (1920).

[4] *J. Am. Chem. Soc.*, **43**, 2563 (1921).

TABLE XV

POTENTIALS IN MILLIVOLTS AT JUNCTIONS OF UNIUNIVALENT CHLORIDE SOLUTIONS AT 25°

Junction	E.M.F. (Obs.) (M. and Y.) Flowing	E.M.F. (Obs.) (L., B. and S.) Stationary	E.M.F. (Calc.) Lewis and Sargent's Equation
HCl (0.1) | KCl (0.1)	26.8	27.8	28.4
HCl (0.01) | KCl (0.01)	25.7	27.2	27.4
HCl (0.1) | LiCl (0.1)	34.9	—	35.8
HCl (0.1) | NH_4Cl (0.1)	28.4	—	28.6
KCl (0.1) | NaCl (0.1)	6.4	—	4.9
NaCl (0.1) | LiCl (0.1)	2.6	—	2.5
HCl (0.01) | NH_4Cl (0.01)	27.0	—	27.4
HCl (0.01) | LiCl (0.01)	33.8	—	34.2
KCl (0.01) | NH_4Cl (0.01)	1.3	—	0.05

A comparison of the results obtained by the flowing and stationary junctions shows of how great importance is the method of forming the junction. The values computed by Lewis and Sargent's formula agree well with the observed values obtained by MacInnes and Yeh except in the cases where potassium chloride solutions were used. This peculiar behavior has not yet been explained. It would appear from these results that the Lewis and Sargent formula may be relied on to give results which will probably not be in error by over one millivolt in very dilute solutions.

Further Considerations of Liquid Junction Potentials at Higher Concentrations: We have already shown from the general formula for cells with and and without transference that such measurements cannot yield any information regarding ind vidual ionic free energies. Perhaps, the situation can be clarified by reconsidering the general equation (194), namely,

$$\mathbf{E}_1 = -\sum_1^s 0.05915 \int_1^2 t_i d\ln m_i - \sum_1^s 0.05915 \int_1^2 t_i d\ln \gamma_i. \qquad (194)$$

We have already shown that the convention that all the "γ_is" equal unity at infinite dilution defines the liquid junction at the limiting condition. But in order to define $\mathbf{E}_1$ under conditions where the "γ_is" do not equal unity, we find that it is necessary to know t_i as a function of γ_i for every ion. It is just this knowledge of γ_i which we have found cannot be obtained from any measurement of cells with or without liquid junctions. Therefore, we cannot employ equation (194) to evaluate $\mathbf{E}_1$ without another purely arbitrary definition, which may have no theoretical value or physical meaning but which may prove useful for numerical calculations.

Such an arbitrary device has been employed by Harned.[1] To define an individual ionic activity coefficient, it is necessary to choose a standard state.

[1] Harned, *J. Phys. Chem.*, **30**, 433 (1926).

Since it is impossible to remove an ion from a solution, it is necessary to refer individual activity coefficients to a standard state. Let the arbitrary state for individual ion activity coefficients be the condition that, at all concentrations, the activity coefficients of the potassium and chloride ions are the same.

On the basis of this definition, Harned was able to show by the graphical integration of the second integral of equation (194) that the observed liquid junction potential agreed with that calculated in the case of the sums of junctions of the types:

$$\mathrm{HCl}(m_0)\,|\,\text{sat. KCl}\,|\,\mathrm{HCl}(m_0),\ \mathrm{MCl}(m),$$
$$\mathrm{MOH}(m_0)\,|\,\text{sat. KCl}\,|\,\mathrm{MOH}(m_0),\ \mathrm{MCl}(m),$$

for considerable concentration ranges. At the same time he showed that any other definition of γ_i would give the same result provided that the values of the product $\gamma_{\mathrm{M}}\gamma_{\mathrm{Cl}}$ were correct. Such calculations are only valuable for checking numerical observations and proving whether the cells employed are reversible or irreversible.

The ideal solution for eliminating liquid junction potentials has been regarded as one which contains the electrolyte at very high concentration, so that most of the transfer across the boundary will be carried out by its ions, and also one whose ions have identical transference numbers. The conditions will obviously reduce the magnitude of the integral $\int_1^2 t_i d\ln m_i$ in equation (194). Potassium chloride forms a 4.8 M saturated solution and its cation transference number is about 0.496. But this does not reduce the numerical value of the second integral. In order for this to be zero γ_{K} and γ_{Cl} must be equal or nearly so. Thus, if we adopt the convention that γ_{K} equals γ_{Cl} then according to equation (194) the second integral will be small, since positive and negative ions have opposite effects. Consequently, $\mathbf{E}_{\mathrm{I}}$ will be small but *small by a purely arbitrary definition.* We thus find that from measurements of cells with liquid junctions or with salt bridges, very little information of a quantitative nature regarding activity coefficients may be expected to be obtained.

Summary of Conclusions Regarding Liquid Junction Potentials: 1. Measurements of cells with or without transference cannot yield any information regarding ionic free energies or activities but only sums of free energies of positive and negative ions and activity products.

2. The ionic free energy or activity requires further definition but such a definition is entirely arbitrary and will lead to no further information regarding the properties of the homogeneous solution phase.

3. Formulas for liquid junction potentials are strictly valid only at infinite dilution. By the use of an arbitrary definition such as the equality of γ_{K} and γ_{Cl} or the equality of $\gamma_{\mathrm{Cl(KCl)}}$ and $\gamma_{\mathrm{Cl(NaCl)}}$ etc., these formulas may be applied to test the consistency of the measurements and reversibility of the cells.

4. Great care should be exercized in the interpretation of the results of the measurements of cells with salt bridges. Only in very special cases where the

possibility of the sums of the two liquid junctions potentials involved approaches zero may such cells yield quantitative results. Indeed, in the latter case, concentration ratios, not activity ratios, are measured.

Some General Considerations Regarding the Theory of Solutions in Its Relation to Activity Coefficients

In the previous discussion, we have presented the thermodynamic properties of salt solutions and have laid particular emphasis upon the activity coefficients, or the deviation factor from the classic laws of ideal solutes. We have developed the theory of Debye and Hückel in considerable detail and found that it yields a limiting law which is valid within the experimental error in the very dilute solutions. We have also pointed out the effect upon the activity coefficient which is caused by considering the ions to have finite sizes. Further, we have discussed Hückel's theory of concentrated solutions which accounts for the linear term in the equation of the activity coefficients, (159), by an assumption regarding the variation of the dielectric constant of the medium. We have pointed out the uncertianties inherent in the last two considerations.

That ionic association is always possible and may depend on the ionic diameters has been shown by Bjerrum [1] in an investigation which we have previously mentioned. Conceptions regarding this phenomenon are somewhat confused. As long as electrostatic forces only are operative, an ion complex is to be regarded as a pair of oppositely charged ions, electrically neutral. Considered statistically, at a given moment, the cross-section of a solution would show that on the average positive and negative ions were closer together than ions of like signs. Such a picture would be different from one in which a definite reaction, or rearrangement of electrons was conceived to take place when two ions combined. In the latter case, a mechanism quite different from the continuous action of electrostatic forces and one which would involve a quantum discontinuity might be conceived. If this is the case, then an undissociated molecule would be different in kind from an associated complex resulting from the operation of the Coulomb's forces only.

These considerations raise a very interesting question. Electrolytes vary in tendency to dissociate from the completely ionized type such as sodium chloride to the very slightly ionized organic acids and bases, providing that we are considering solutions which are not infinitely dilute. In the case of symmetrical ions of the " noble gas type " structure, it appears that only electrostatic forces are operative. Little tendency to form definite combinations other than the electrostatic associated type is to be observed with solutions containing alkali, alkaline earth and halide ions. A tendency to form associated ion complexes always acts to lower the activity coefficient. For this reason, as we pass from the " noble gas type " ions of almost perfect electron symmetry to ions such as the nitrate, iodate and hydroxide, which have an in-

[1] Bjerrum, *Det Kgl. Danske Videnskapernens Selskab.*, **7**, 9 (1926).

creasingly less symmetry, or ions which are dipoles, a greater tendency to form associated groups is observable. Association of these ions, of course, becomes apparent when the electrical field intensity becomes greater in the more concentrated solutions, and under these conditions specific reactions become noticeable. Thus, we find at a given concentration,

$$\gamma_{NaCl} > \gamma_{KCl}; \qquad \gamma_{NaIO_3} = \gamma_{KIO_3}; \qquad \gamma_{NaOH} < \gamma_{KOH},$$

which shows that the sodium ion tends to lower the activity coefficient of a hydroxide solution to a greater extent than the potassium ion. Thus, in the presence of the electrical field of the lithium or sodium ion, there will be a greater deformation or polarization of the hydroxyl ion than that caused by the potassium ion. This effect parallels the tendency of ions to form associated complexes, and increases the probability of the formation of undissociated molecules. Many organic electrolytic ions which combine readily with hydrogen or hydroxyl ions show a behavior similar to that of the hydroxyl ion. For example, we have pointed out that

$$\gamma_{HOH(KCl)} > \gamma_{HOH(NaCl)} > \gamma_{HOH(LiCl)}.$$

Acetic acid, monochloro-acetic and dichloro-acetic acids, mono- and dimethylamine exhibit the same behaviour in these salt solutions.[1]

From the fact that weak acids and hydroxides form the large class of weak electrolytes, we are led to think that the reaction to form undissociated molecules with organic anions or cations is largely due to a specific reaction with the hydrogen or hydroxyl ion involving a quantum change.

A very important contribution to the study of the specific effects of the presence of ions of different kinds upon the activity coefficients of other electrolytes has been made by Brönsted and his collaborators. These investigations have revealed many specific behaviors in dilute solutions of electrolytes brought about by the presence of other electrolytes. The data were obtained principally from the measurements of the solubilities of higher order cobalt compounds in salt solutions. As a result, Brönsted has proposed a theory of ionic interaction which rests on the postulate that " in dilute salt solution of constant total concentration, ions will be uniformly influenced by ions of like sign." The theory upon which this principle rests is that in dilute solutions specific electrical effects take place between the ions. In dilute solutions, only those ions of unlike sign would approach closely enough to one another to produce these effects. Brönsted regards these electrical effects as different from the " salting out or solvent effect " and for the purposes of developing his theory considers the activity coefficient of an ion in the presence of other ions as made up of a number of parts. Thus

$$\gamma_{H(KNO_3)} = \gamma_{H(K)} \cdot \gamma_{H(NO_3)} \cdot \gamma_{(K)} \cdot \gamma_{NO_3},$$

[1] Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926); Harned and Douglas, *J. Am. Chem. Soc.*, **48**, 3095 (1926); Harned. *J. Am. Chem. Soc.*, **49**, 1 (1927). *Trans. Farad. Soc.*, **23**, 462 (1927). *Trans. Am. Electrochem. Soc.*, **51**, 571 (1927); Harned and Hawkins, *J. Am. Chem. Soc.*, **50**, 86 (1928); Harned and Robinson, *J. Am. Chem. Soc.*, **50**, 3157 (1928).

where $\gamma_{H(K)}$, $\gamma_{H(NO_3)}$ are the coefficients of interaction, and γ_K, γ_{NO_3} are the salting out coefficients of the potassium and nitrate ions on the hydrogen ion. Similarly, in a sodium nitrate solution

$$\gamma_{H(NaNO_3)} = \gamma_{H(Na)} \cdot \gamma_{H(NO_3)} \cdot \gamma_{Na} \cdot \gamma_{NO_3}.$$

Now, according to the postulate of the theory

$$\gamma_{H(K)} = \gamma_{H(Na)}$$

and, consequently,

$$\frac{\gamma_{H(NaNO_3)}}{\gamma_{H(KNO_3)}} = \frac{\gamma_{(Na)}}{\gamma_{(K)}}.$$

Although we can criticize this theory upon the grounds developed in the last section regarding the arbitrariness of this use of individual ion activity coefficients, Brönsted has been able to predict some specific behaviors which are unquestionably valid experimentally.

The idea of salting out coefficients leads us to the further consideration of the effects upon the activity coefficients of the ions which are due to the interaction between the ions and the solvent. There are two ways of regarding ionic hydration. The first is to assume the formation of ion hydrates of definite composition, and apply the law of mass action. This method has been employed by Bjerrum for the calculation of hydration values of ions from activity coefficients or vice versa. Other applications of the theory are contained in the papers of Schreiner.[1]

Around the electrified particles or ions, there is unquestionably a very great tendency for the solvent molecules to crowd. This is evidenced by the fact that in the case of solutions of salts such as potassium chloride, there is a considerable shrinkage in volume which must be largely due to the contraction of the water molecules themselves. But this is not always true, since we find that the water volume in lithium iodide solutions is greater than that in pure water, or that an actual expansion takes place. From the data of Baxter and Wallace,[2] we find that the volume of water in concentrated halide solutions of a given strength is in the order

$$V_{LiI} > V_{LiBr} > V_{LiCl} > V_{NaI} > V_{NaBr} > V_{NaCl} > V_{KI} > V_{KBr} > V_{KCl}.$$

This is exactly the order of the activity coefficients in a given strength of these solutions. Further, it is exactly the order which we find for the dissociation of water itself in the presence of these salts at a given concentration.

A consistent point of view in regard to these parallel behaviors can be obtained from the following considerations. If we consider electrostatic

[1] Bjerrum, *Z. anorg. Chem.*, **109**, 275 (1920); Schreiner, *ibid.*, **115**, 181 (1921); **116**, 102 (1921); **121**, 321 (1922); A discussion of this theory by Harned is contained in Chap. XII of Taylor, Treatise on Physical Chemistry (pp. 775–779). Van Nostrand and Co., New York (1924).

[2] Baxter and Wallace, *J. Am. Chem. Soc.*, **38**, 70 (1910).

forces of attraction only, then according to equation (147), the activity coefficients of all electrolytes decrease with increasing ionic strength. The effect of the sizes of the ions which corresponds to repulsive forces between the absolute ionic centers acts in the oppoiste direction to the attractive forces as shown by equation (156). Polarization by deformation of the solvent molecules brought about by the electrical fields of the ions will have the effect of reducing the attractive forces between the ions which is the same as increasing the repulsive forces. Both the A and B constants in equation (159) would be the result of repulsive forces between the ions.

The order of the observed results accords with this conception. Lithium iodide which causes an expansion of the water molecules, causes the greatest dissociation of these molecules, and possesses the highest activity coefficient of the alkali halides. All others follow in the proper order. Similar views to this one have been expressed by Harned and Douglas.[1]

Such a theory does not necessarily conflict with Hückel's theory since the influences of the ions on the water molecules may change the macroscopic dielectric constant of the medium. However, we would contend that this solvent action would be the principal cause of the variation of the dielectric constant.

Standard Electrode Potentials

On account of the very important properties of the free energy, the determination of the free energies of chemical substances and the free energy increments of reactions constitutes one of the most important and useful developments in chemistry. It has previously been shown that measurements of the electromotive forces of galvanic cells under conditions of reversibility afford a very important means of obtaining the free energy changes of cell reactions. In order to collect the accurate available data in a convenient and useful system, and thus make them part of the general systematization of free energy data, it has been customary to divide cells into two electrode parts, and construct a table of electrode potentials.

Since 1889, when Nernst developed his osmotic theory and his well-known formula for the concentration cell, the importance of obtaining standard electrode potentials has been realized. In 1900, Wilsmore [2] published a table of electrode potentials. In 1911, Abegg, Auerbach and Luther,[3] published a more comprehensive table of similar data. The development up to that time may be regarded as the extensive period. In later years, many electrode potentials have been determined with greater precision. The principal advances during the last fifteen years have been made with few exceptions by G. N. Lewis and his colleagues. The chief factors leading to these recent developments are the more precise measurements of the activities of electrolytes, the

[1] Harned and Douglas, *J. Am. Chem. Soc.*, **48**, 3095 (1926).

[2] *Z. physik. Chem.*, **35**, 291 (1900).

[3] "Messungen elektromotorische Kräfte galvanischer Ketten," Abhandlungen der deutschen Bunsengesellschaft, No. 5. Halle, 1911.

ingenious and accurate method of Lewis and Kraus for obtaining the potentials of the alkali metal electrodes, and the use of metals in a finely divided form as electrodes. These interesting measurements and the calculations of the electrode potentials have been discussed in detail by Lewis and Randall who have also compiled a table of the standard molal electrode potentials at 25°.[1] The present discussion will be confined to the consideration of the necessary conventions, and to the discussion of some methods of calculation.

Conventions and Nomenclature, and Table of Standard Electrode Potentials:[2] According to equation (45), we found that for any chemical reaction a change in free energy referred to a normal state is given by

$$\Delta F - \Delta F_0 = RT ln \frac{a_{A'_1}^{n'_1} \cdots a_{A'_2}^{n'_2} \cdots}{a_{A_1}^{n_1} \cdots a_{A_2}^{n_2} \cdots}. \tag{45}$$

By adopting the convention that the electromotive force of the cell is positive when the positive current flows from left to right, we found that a decrease in free energy, $(-\Delta F)$, equals **NEF**, and, therefore, $(-\Delta F_0)$ equals $\mathbf{NE_0F}$, where $\mathbf{E_0}$ is a standard electromotive force. From these considerations, we obtain

$$\mathbf{E} = \mathbf{E_0} - \frac{RT}{\mathbf{NF}} ln \frac{a_{A'_1}^{n'_1} \cdots a_{A'_2}^{n'_2} \cdots}{a_{A_1}^{n_1} \cdots a_{A_2}^{n_2} \cdots}. \tag{205}$$

This equation is true for any cell reaction. Now, we choose as a normal state the condition that the activities equal unity, under which condition **E** will equal $\mathbf{E_0}$.

Any cell reaction may be broken up into two parts, and the electromotive force of the corresponding cell may be divided into two electrode potentials. For example, the reaction

$$\tfrac{1}{2}Zn + H^+(1M) = \tfrac{1}{2}Zn^{++}(1M) + \tfrac{1}{2}H_2$$

may be split up into

$$(a) \quad \tfrac{1}{2}Zn = \tfrac{1}{2}Zn^{++} + \Theta; \qquad (b) \quad H^+ + \Theta = \tfrac{1}{2}H_2$$

or

$$(a) \quad \tfrac{1}{2}Zn = \tfrac{1}{2}Zn^{++} + \Theta; \qquad (c) \quad \tfrac{1}{2}H_2 = H^+ + \Theta,$$

where Θ represents one Faraday of electrons. The same convention is adopted for the single electrode potentials as for the cells, namely, that its electromotive force is positive when positive current flows from left to right. For the above electrode processes, then, we obtain

$$\left.\begin{aligned} (a) \quad \mathbf{E} &= \mathbf{E_0} - \frac{RT}{\mathbf{F}} ln a_{Zn^{++}}, \\ (b) \quad \mathbf{E} &= \mathbf{E_0} - \frac{RT}{\mathbf{F}} ln \frac{p^{1/2}}{a_{H^+}}, \\ (c) \quad \mathbf{E} &= \mathbf{E_0} - \frac{RT}{\mathbf{F}} ln \frac{a_{H^+}}{p^{1/2}}, \end{aligned}\right\} \tag{206}$$

where p is the hydrogen pressure.

[1] Lewis and Randall, Thermodynamics, McGraw-Hill Book Co. (1923).

[2] Lewis, *J. Am. Chem. Soc.*, **35**, 1 (1913).

No method is known for the evaluation of the absolute potential of an electrode, and, for this reason, a standard reference potential must be chosen. It is customary at the present time to refer all electrodes to the hydrogen electrode at one atmosphere pressure in a solution of hydrogen ions of unit activity.[1] Thus, for the hydrogen electrode, $\mathbf{E}_0 = 0$, at all temperatures. By referring all electrodes to the hydrogen electrode, either by direct or indirect comparison, the tables of standard electrode potentials at 25° have been compiled. In Table XV, Part I, are given the values obtained by Lewis and Randall, taken for the most part from the investigations of Lewis and his associates. References to the original literature are given below the table. The electrode reactions are so arranged that the values for the free energies are equal simply to $(-\mathbf{E}_0\mathbf{F})$. In Part II of the Table are given some values for the electrode potentials of other elements taken from the compilation of

TABLE XV[2]

PART I

Standard Electrode Potentials at 25°

	Electrode	Electrode Reaction	$\mathbf{E}_0$
1.	Li|Li$^+$	Li = Li$^+$ + Θ	2.9578
2.	Rb|Rb$^+$	Rb = Rb$^+$ + Θ	2.9242
3.	K|K$^+$	K = K$^+$ + Θ	2.9224
4.	Na|Na$^+$	Na = Na$^+$ + Θ	2.7125
5.	Zn|Zn^{++}	$\frac{1}{2}$Zn = $\frac{1}{2}$Zn^{++} + Θ	0.7581
6.	Fe|Fe^{++}	$\frac{1}{2}$Fe = $\frac{1}{2}$Fe^{++} + Θ	0.441
7.	Cd|Cd^{++}	$\frac{1}{2}$Cd = $\frac{1}{2}$Cd^{++} + Θ	0.3976
8.	Tl|Tl$^+$	Tl = Tl$^+$ + Θ	0.3363
9.	Sn|Sn^{++}	$\frac{1}{2}$Sn = $\frac{1}{2}$Sn^{++} + Θ	0.136
10.	Pb|Pb^{++}	$\frac{1}{2}$Pb = $\frac{1}{2}$Pb^{++} + Θ	0.122
11.	Fe|Fe^{+++}	$\frac{1}{3}$Fe = $\frac{1}{3}$Fe^{+++} + Θ	0.045
12.	Pt|H$_2$|H$^+$	$\frac{1}{2}$H$_2$ = H$^+$ + Θ	0
13.	Cu|Cu^{++}	$\frac{1}{2}$Cu = $\frac{1}{2}$Cu^{++} + Θ	− 0.3448
14.	Hg|Hg$_2^{++}$	Hg = $\frac{1}{2}$Hg$_2^{++}$ + Θ	− 0.7986
15.	Ag|Ag$^+$	Ag = Ag$^+$ + Θ	− 0.7995
16.	Pt|S^{--}|S (rhomb)	$\frac{1}{2}$S^{--} = $\frac{1}{2}$S (rhomb) + Θ	0.51
17.	Pt|OH$^-$|O$_2$	OH$^-$ = $\frac{1}{4}$O$_2$ + $\frac{1}{2}$H$_2$O + Θ	− 0.3976
18.	Pt|I$^-$|I$_2$ (s)	I$^-$ = $\frac{1}{2}$I$_2$ (s) + Θ	− 0.5357
19.	Pt|Br$^-$|Br (l)	Br$^-$ = $\frac{1}{2}$Br$_2$ (l) + Θ	− 1.0659
20.	Pt|Cl$^-$|Cl$_2$ (g)	Cl$^-$ = $\frac{1}{2}$Cl$_2$ (g) + Θ	− 1.3594
21.	Hg|HgCl|Cl$^-$	Hg + Cl$^-$ = HgCl + Θ	− 0.2700
22.	Ag|AgCl|Cl$^-$	Ag + Cl$^-$ = AgCl + Θ	− 0.2245
23.	Hg|Hg$_2$SO$_4$|SO$_4^{--}$	Hg + $\frac{1}{2}$SO$_4^{--}$ = $\frac{1}{2}$Hg$_2$SO$_4$ + Θ	− 0.6213
24.	Pt|H$_2$|OH$^-$	$\frac{1}{2}$H$_2$ + OH$^-$ = H$_2$O (l) + Θ	0.8280
25.	Hg|HgO|OH$^-$	$\frac{1}{2}$Hg + OH$^-$ = $\frac{1}{2}$HgO + $\frac{1}{2}$H$_2$O + Θ	− 0.0984

[1] By activity of hydrogen ion is usually meant the square root of the activity product of hydrochloric acid. Similarly, in measuring any electrode potential activity products should be employed. This answers any objection to the calculations which might result from the use of individual ion activity coefficients.

[2] More recently, values of the standard electrode potentials have been compiled by Gerke, International Critical Constant Tables, Vol. VI, p. 332, McGraw-Hill Book Co., New York (1930).

REFERENCES TO PART I, TABLE XV

(1) (3) Lewis and Keyes, *J. Am. Chem. Soc.*, **34**, 119 (1912); **35**, 340 (1913).
(2) Lewis and Argo, *ibid.*, **37**, 1983 (1915).
(4) Lewis and Kraus, *ibid.*, **32**, 1459 (1910).
(5) (7) Horsch, *ibid.*, **41**, 1787 (1919).
(8) Lewis and von Ende, *ibid.*, **32**, 732 (1910).
(9) Noyes and Toabe, *ibid.*, **39**, 1537 (1917).
(13) (23) Lewis and Lacy, *ibid.*, **36**, 804 (1914).
(14) Linhart, *ibid.*, **38**, 2356 (1916).
(15) Noyes and Braun, *ibid.*, **34**, 1016 (1912).
(16) Sammet, *Z. physik. Chem.*, **53**, 641 (1905); Maitland, *Z. Elektrochem.*, **12**, 263 (1906).
(19) Lewis and Storch, *J. Am. Chem. Soc.*, **39**, 2544 (1917).
(20) Lewis and Rupert. *ibid.*, **33**, 299 (1911).
(21) Lewis, Brighton and Sebastian, *ibid.*, **39**, 2245 (1917).
(23) Randall and Cushman, *ibid.*, **40**, 393 (1918).
(24) Lorenz and Böhi, *Z. physik. Chem.*, **66**, 733 (1909).
(25) Brönsted, *Z. physik. Chem.*, **65**, 84 (1909); **65**, 744 (1909). Ming Chow, *J. Am. Chem. Soc.*, **42**, 488 (1920).

PART II

Electrode	Electrode Reaction	E_0
1. $Ba\|Ba^{++}$	$\frac{1}{2}Ba = \frac{1}{2}Ba^{++} + \Theta$	2.8
2. $Sr\|Sr^{++}$	$\frac{1}{2}Sr = \frac{1}{2}Sr^{++} + \Theta$	2.7
3. $Ca\|Ca^{++}$	$\frac{1}{2}Ca = \frac{1}{2}Ca^{++} + \Theta$	2.5
4. $Mg\|Mg^{++}$	$\frac{1}{2}Mg = \frac{1}{2}Mg^{++} + \Theta$	1.55
5. $Mn\|Mn^{++}$	$\frac{1}{2}Mn = \frac{1}{2}Mn^{++} + \Theta$	1.0
6. $Cr\|Cr^{+++}$	$\frac{1}{3}Cr = \frac{1}{3}Cr^{+++} + \Theta$	0.5
7. $In\|In^{+++}$	$\frac{1}{3}In = \frac{1}{3}In^{+++} + \Theta$	0.35
8. $Co\|Co^{++}$	$\frac{1}{2}Co = \frac{1}{2}Co^{++} + \Theta$	0.29
9. $Ni\|Ni^{++}$	$\frac{1}{2}Ni = \frac{1}{2}Ni^{++} + \Theta$	0.22
10. $Sb\|Sb^{+++}$	$\frac{1}{3}Sb = \frac{1}{3}Sb^{+++} + \Theta$	− 0.1
11. $Bi\|Bi^{+++}$	$\frac{1}{3}Bi = \frac{1}{3}Bi^{+++} + \Theta$	− 0.2
12. $As\|As^{+++}$	$\frac{1}{3}As = \frac{1}{3}As^{+++} + \Theta$	− 0.3
13. $Pd\|Pd^{++}$	$\frac{1}{2}Pd = \frac{1}{2}Pd^{++} + \Theta$	− 0.82
14. $Au\|Au^{+}$	$Au = Au^{+} + \Theta$	− 1.5
15. $Pt\|F^{-}\|F_2$	$F^{-} = \frac{1}{2}F_2 + \Theta$	− 1.9

Abegg, Auerbach, and Luther. These values are of a much lower order of accuracy.[1]

Some Calculations of Standard Electrode Potentials: In order to illustrate the methods of evaluating standard electrode potentials, we shall consider two typical calculations made by Lewis and Randall.

The $Hg|HgCl\ (s)|Cl^{-}$ *Electrode.* Many measurements of the cell

$$H_2|HCl\ (0.1)|HgCl|Hg$$

by different investigators give 0.3989 for **E**. By equation (205), since the activities of the solid phases are unity,

$$\mathbf{E} = \mathbf{E}_0 - \frac{RT}{\mathbf{F}} ln a_{\mathbf{H}} a_{\mathbf{Cl}} = \mathbf{E}_0 - 0.1183 \log m\gamma.$$

[1] The values of the standard electrode potentials in this table are the same as those in the first edition of this Treatise published in 1924. Although several minor changes could be made, it seems advisable to wait for a few years until sufficient data are available to make possible a considerable improvement. The difficulties regarding the evaluation of liquid junction potentials also cause a very considerable uncertainty regarding many of the results.

Lewis and Randall take the activity coefficient of the acid to be 0.814 at 0.1 molal. Using this value, E_0 equals 0.2700, which is the electromotive force of the cell when both a_H and a_{Cl} equal unity, or the standard electromotive force of the cell. If the cell is divided into

$$(a) \quad Pt|H_2|H^+ \quad \text{and} \quad (b) \quad Hg|HgCl|Cl^-,$$

then it is obvious that $0.2700 = E\ (a) - E\ (b)$, and since $E\ (a) = 0$,

$$Hg|HgCl|Cl^-; \qquad E_0 = -0.2700.$$

From this value, the electromotive force of the electrode Hg|HgCl|KCl (0.1) may be computed by the equation

$$E = E_0 - \frac{RT}{F} ln \frac{1}{a_{Cl}}.$$

Lewis and Randall take 0.0794 as the activity of the chloride ion ($\sqrt{a_K a_{Cl}}$) in 0.1 molal potassium chloride, and obtain

$$Hg|HgCl|KCl\ (0.1); \qquad E = -0.3351.$$

The Sodium Electrode. Lewis and Kraus measured the cell

$$Na\ (s)|NaI \text{ in } C_2H_5NH_2|0.206 \text{ per cent Na-amalgam}$$

and obtained 0.8453 for its electromotive force. They found that the sodium electrode under these conditions was far more reproducible than any other metal electrode. Consequently,

$$Na\ (s)|Na\ (0.206 \text{ per cent amalgam}); \qquad E = 0.8453.$$

In their investigation, Lewis and Kraus employed cells with liquid junctions. Lewis and Randall, in a more recent calculation, have shown that these liquid junctions may be avoided. Thus, from the results of Allmand and Polack,[1] Lewis and Randall obtained by interpolation

$$Na\ (0.206 \text{ per cent amalgam})|NaCl\ (1.022)|HgCl|Hg; \qquad E = 2.1582$$

and, therefore, by combination

$$Na\ (s)|NaCl\ (1.022)|HgCl|Hg; \qquad E = 3.0035.$$

The activity coefficient of 1.022 molal sodium chloride is taken to be 0.650, whence

$$Na\ (s)|Na^+\ (1)||Cl^-\ (1)|HgCl|Hg; \qquad E_0 = 2.9825.$$

It has already been found that the electromotive force of the standard calomel electrode is -0.2700, and, consequently,

$$Na\ (s)|Na^+; \qquad E_0 = 2.7125.$$

This ingenious method, which has more recently been applied in determining the other alkali metal electrodes, constitutes the most important advance made in the last fifteen years in the determination of standard electrode potentials.

Electrode Potentials and Equilibrium Constant: From equation (45) it follows that at equilibrium, since $\Delta F = 0$,

$$\Delta F_0 = -RTlnK,$$

where K is the equilibrium constant, and, therefore, at 25°,

$$E_0 = \frac{RT}{NF} lnK = \frac{0.05915}{N} \log K. \tag{207}$$

[1] *J. Chem. Soc.*, **115**, 1020 (1919).

This important equation permits the direct evaluation of the equilibrium constant of a reaction from the table of standard electrode potentials.

(*a*) *The Ionic Product of Water at 25° C.;* From Table XV we find that

$$\tfrac{1}{2}H_2 = H^+ + \Theta; \qquad E_0 = 0$$

and

$$\tfrac{1}{2}H_2 + OH^- = H_2O\ (l) + \Theta; \qquad E_0 = 0.8280.$$

Subtracting the second of these equations from the first, we obtain

$$H_2O\ (l) = H^+ + OH^-; \qquad E_0 = -0.8280$$

and, by equation (207), since the liquid has unit activity,

$$-0.8280 = 0.05915 \log a_H a_{OH} = 0.05915 \log K_w,$$

whence

$$K_w = 1.005 \times 10^{-14}$$

at 25°.

(*b*) *Solubility Product:* From the Table we find that

$$Ag + Cl^- = AgCl + \Theta; \qquad E_0 = -0.2245$$

and

$$Ag = Ag^+ + \Theta; \qquad E_0 = -0.7995,$$

whence

$$Ag^+ + Cl^- = AgCl; \qquad E_0 = 0.5750.$$

By equation (207), we obtain

$$0.5750 = 0.05915 \log \frac{1}{a_{Ag} a_{Cl}} = 0.05915 \log \frac{1}{S}$$

from which

$$S = 1.90 \times 10^{-10}$$

at 25°.

(*c*) *Replacement Equilibrium*: From reactions (5) and (12) in Table XV, we find that

$$\tfrac{1}{2}Zn + H^+ = \tfrac{1}{2}H_2 + \tfrac{1}{2}Zn^{++}; \qquad E_0 = 0.7581$$

and by equation (207)

$$0.7581 = 0.05915 \log K = 0.05915 \log \frac{a_{Zn}{}^{1/2} p_{H_2}{}^{1/2}}{a_H}$$

from which we find that

$$K = 6.45 \times 10^{12}.$$

If we had a solution containing zinc and hydrogen ions at unit activity, and immersed in it a strip of pure zinc, it may be calculated from this value of the equilibrium constant that a pressure of 2.53×10^{25} atmospheres would be required to prevent the formation of hydrogen.

Effect of Pressure on Electromotive Force: The pressure coefficient of free energy of a system at constant composition and at constant temperature has been shown to be in general

$$\left[\frac{\partial F}{\partial p}\right]_{N,\,T} = V,$$

where V is the volume of the system. For a variation of an increment in free energy of a process, we obtain

$$\left[\frac{\partial \Delta F}{\partial p}\right]_{N,\ T} = \Delta V, \tag{208}$$

where ΔV is the volume change of the process. In an electrode or a cell process involving the passage of one Faraday, $\Delta F = -\mathbf{EF}$, and, therefore,

$$\left[\frac{\partial \mathbf{E}}{\partial p}\right]_{T,\ N} = -\frac{\Delta V}{\mathbf{F}}. \tag{209}$$

Let us now apply this equation to the cell

$$H_2 \,|\, HCl\ (0.1M) \,|\, HgCl \,|\, Hg,$$

which possesses a gas electrode, subject to large changes in volume. The cell reaction, corresponding to the passage of one Faraday, is

$$\tfrac{1}{2}H_2 + HgCl = HCl\ (0.1) + Hg$$

and the total change in volume is

$$\Delta V = (\overline{V}_{HCl} + V_{Hg}) - (\tfrac{1}{2}V_{H_2} + V_{HgCl}). \tag{210}$$

For small pressures, and small changes in pressure, $\frac{1}{2}V_{H_2} = \frac{1}{2}\frac{RT}{p}$, and, if we neglect the volume changes of the solids and solutions which are small compared with that of the gas,

$$\partial \mathbf{E} = \frac{RT}{2\mathbf{F}}\,\partial ln p \tag{211}$$

is obtained by means of equation (209). The change in electromotive force, $\Delta\mathbf{E}$, produced by a change in pressure from one atmosphere to p atmospheres is

$$\Delta \mathbf{E} = \int_1^p \frac{RT}{2\mathbf{F}}\,\partial ln p = \frac{RT}{2\mathbf{F}}\,ln p. \tag{212}$$

$\Delta\mathbf{E}$ at low pressures is really the change in electromotive force at the hydrogen electrode. If the process at the hydrogen electrode is reversible, then $\mathbf{E}$ should vary with the hydrogen pressure, p, according to this equation. Measurements of this variation with pressure afford a simple means of testing the reversibility of hydrogen or other gas electrodes. Lewis and Randall,[1] Ellis,[2] and Loomis and Acree[3] have found that for small changes of pressure this equation is valid. Equation (212) has been employed for correcting electromotive forces of cells with a hydrogen electrode to one atmosphere hydrogen pressure.

[1] *J. Am. Chem. Soc.*, **36**, 1969 (1914).
[2] *J. Am. Chem. Soc.*, **38**, 737 (1916).
[3] *J. Am. Chem. Soc.*, **38**, 2391 (1916).

More recently, Hainsworth and MacInnes[1] have measured the electromotive force of the hydrogen-calomel cell at different pressures up to 400 atmospheres. They employed the equation of state of Keyes[2] for the hydrogen pressure, and took into consideration the factors involving the changes in $\overline{V}_{HCl}$, V_{Hg} and V_{HgCl} with the pressure. Their calculated results agreed very closely with the observed results up to 50 atmospheres hydrogen pressure, above which a slight uniform deviation appeared, which they attributed to the solubility of hydrogen.

The effect of high pressures on the electromotive forces of many cells not containing gas electrodes forms an important part of the "Piezochemical Studies" of Cohen and his colleagues.[3]

Some General Considerations: A glance at the table of standard electrode potentials which represents the best results of many investigators during the last thirty years will show that it is far from being very comprehensive. Apart from the determination of the standard electrode potentials, there remains the study of the variation of the electrode potentials with the concentration, the pressure and the temperature. The recent accurate studies of concentration cells, freezing point lowerings, etc., have furnished the data of the type necessary for computing the variation with the concentration. This work has been discussed in detail. The temperature variations of both activities and electrode potentials constitute a very important field for investigation. Although the methods are well known, there are not sufficient accurate data available to warrant a systematization. Further development awaits data on partial specific heats, and heat contents of the ions and their variations with the temperature; the electromotive forces, the heat content changes of cell reactions and their variations with the temperature. Such data will lead to a more and more complete knowledge of reversible processes involving solutions, of cell reaction equilibria, and the inner equilibria in solutions.

Theories of Electrode Processes

Thermodynamics alone yields no knowledge regarding the inner constitution of a system. In order to apply thermodynamic equations to a system, it is necessary to have an equation of state for that system and, if such an equation is to be other than purely empirical, it must rest on a knowledge or hypotheses regarding the inner constitution of the system. Nor does thermodynamics give the desired information regarding the inner mechanism of reactions, or the nature of processes occurring at electrodes. It will be of interest now to consider briefly some theories outside the domain of exact thermodynamics which have been employed to account partially for the production of galvanic electricity and the mechanism of electrode processes.

Standard Electrode Potentials of the Elements and Atomic Numbers: That the standard molal electrode potential is a fundamental property of an element becomes evident upon inspection of Fig. 23, wherein the values of the electrode potentials of the elements given in Table XV are plotted against the atomic numbers. Well-marked periodicity is observable. The result is

[1] *J. Am. Chem. Soc.*, **44**, 1021 (1922); **46**, 1437 (1924).

[2] *Proc. Nat. Acad. Sci.*, **3**, 323 (1917); *J. Am. Chem. Soc.*, **46**, 589 (1919).

[3] These contributions occur in *Z. physik. Chem.* from 1909 to the present time. We may cite "Piezochemische Studien XX," Cohen, Ishikawa, and Moesveld, *Z. physik. Chem.*, **105**, 155 (1923).

approximate owing to the many variables involved, and to the somewhat arbitrary manner in which unit activity of the electrolytes has been defined.

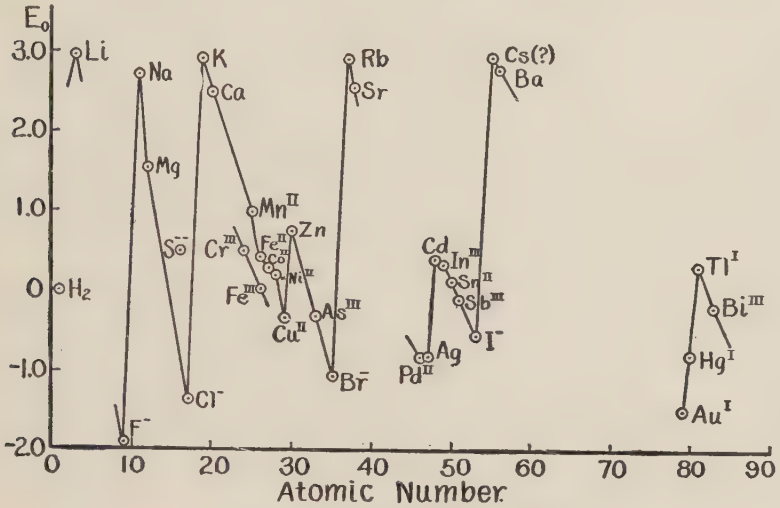

FIG. 23. Molal Electrode Potentials

In Table XV, the electrode reactions have been written as a reaction involving the formation of electrons. Since the free energy decrease of the reaction: $Li = Li^+ + \Theta$ is greater than that of the reaction: $Ag = Ag^+ + \Theta$, we may say that lithium has a greater tendency to form ions and electrons than silver.[1] Similarly, the bromide ion has a greater tendency to form electrons and the element than the chloride ion. In plotting these results, elements which form cations have been compared to the anions, and not to the elements which form anions. That is to say, all electrode processes are taken in the direction of electron formation. Considered in this way, the halogen and sulphide ion electrode potentials fall into well-defined positions. Viewed from the standpoint of atomic theory, we are in this way comparing the tendency of electron shells to give off electrons.

The more electropositive the element, the greater its tendency to form ions and electrons. The more electronegative the element, the greater its tendency to react with an electron to form the anion. If these simple equations represent the true electrode processes, then the electrode potentials are a relative measure of the free energy decrease or affinity of these reactions. This idea was embodied in the theory of "electro-affinity" of Abegg and Bodländer.[2]

[1] It must be borne in mind in the present discussion that the ions are in aqueous solution and at unit activity.

[2] *Z. anorg. Chem.*, **20**, 453 (1899).

The Electrical Double Layer and Osmotic Theory: From the preceding considerations, it appears that all metals have a tendency to go into solution to form cations. Nernst [1] regarded such a tendency as being caused by the "electrolytic solution pressure" of the metal. When a metal such as zinc is immersed in water or in a solution of a salt, its electrolytic solution pressure, which may be very high, tends to form ions of the metal in the solution. In so doing it carries positive charges into the solution which becomes positively charged, and, consequently, leaves the metal negatively charged. This electrical double layer of negative charges on the metal surface and positive charges in the solution near the metal sets up an electrostatic field of great intensity which retards further passage of the metal into the solution. This layer is regarded as being the underlying cause of contact differences of potential at such surfaces.[2]

When a metal is immersed in a solution containing its ions, the factors which determine the electromotive force at the boundary are, according to Nernst, the electrolytic solution pressure of the metal and the osmotic pressure of the metallic ions. Thus, if the solution pressure is greater than the osmotic pressure, the electrode will be charged negatively to the solution, and, vice versa, if the osmotic pressure of the ion is greater than the solution pressure of the metal. From these postulates, Nernst showed that the electrode potential of a metal would be given by the equation

$$\mathbf{E} = \frac{RT}{\mathbf{NF}} ln \frac{P}{\pi},$$

where P is the solution pressure of the metal and π is the osmotic pressure of its ions.

The Debye and Hückel theory gives us an insight into the nature of the Helmholtz double layer. For, consider an electrode immersed in a solution at zero potential extending an infinite distance from the electrode, and let ψ be the potential difference between the solution and electrode. Due to this potential the ions will be distributed in a definite way under conditions of equilibrium. Take x as a coördinate perpendicular to the electrode surface. According to equation (128)

$$\frac{\partial^2 \psi}{\partial x^2} = \kappa^2 \psi. \tag{213}$$

This equation has a solution of the form

$$\psi = \Psi e^{-\kappa x}, \tag{214}$$

where Ψ includes the integration constant. By equations (123) and (128),

[1] *Z. physik. Chem.*, **4**, 150 (1889).

[2] The electrical double layer theory had been employed by Lippmann (*Pogg. Ann.*, **149**, 547 (1873); *Wied. Ann.*, **11**, 316 (1880), and by Helmholtz (Helmholtz, Ges. Abh., **1**, 925) in order to explain capillary electrical phenomena

we find that

$$-\frac{4\pi\rho}{D} = \nabla\cdot\nabla\psi = \kappa^2\psi,$$

whence

$$\rho = -\frac{D\kappa^2}{4\pi}\Psi e^{-nx}. \tag{214}$$

This is an expression for the electrical density at a distance x from the electrode and is similar to equation (136). As x equals successively $1/\kappa$, $2/\kappa$, $3/\kappa$, etc., ρ becomes proportional to e^{-1}, e^{-2}, e^{-3}, etc. $1/\kappa$ then is a measure of the thickness of the Helmholtz double layer, which as a consequence is a function of the concentration, the dielectric constant and the temperature.

Smits' Theory of Electrode Equilibrium: The net effect of an electrode reaction of a metal is given by the reaction:

$$\mathrm{Me} = \mathrm{Me}^{\nu+} + \nu\Theta.$$

This represents a process but gives no insight into the nature of the state of the system when the metal is in equilibrium with a solution of its ions. In accord with the theory of Nernst, it has usually been supposed that the heterogeneous equilibrium between the metal and the solution would be represented by the simple equation

$$\mathrm{Me}_s \rightleftharpoons \mathrm{Me}_l^{\nu+} + \nu\Theta,$$

where $\mathrm{Me}_l^{\nu+}$ is in the solution phase, and Me_s is the solid metal. The true nature of the state of such an equilibrium is at present a matter of speculation.

As a part of the development of his theory of allotropy, Smits [1] has proposed a theory of electromotive force of metal-solution boundaries, which, although highly conjectural, is of particular interest when irreversible electromotive forces are considered. In general, the fundamental proposition of Smits' theory is that all phases, even a phase of one component, such as orthorhombic sulphur, or red phosphorus, is itself complex, or composed of two or more "pseudo-components" which may be molecules, ions, electrons, etc. These pseudo-components may or may not be in stable equilibrium in the phase. The behavior of the phase will depend on its inner equilibrium, and the extent to which this inner equilibrium may be displaced. This idea will become clear when we consider its application to the supposed inner equilibrium which exists between a metal and a solution containing ions of the metal.

The choice of the pseudo-components of a metal phase is somewhat arbitrary. Of the many possible kinds of inner equilibria of the solid metal phase, we may select

$$\mathrm{Me}_s \rightleftharpoons \mathrm{Me}_s^{\nu+} + \nu\Theta,$$

where the pseudo-components are metal molecules or atoms, metallic ions, and electrons. The subscript "s" refers to the solid state, and, consequently, the above equation represents a homogeneous reaction. When the metal is brought into contact with the solution, all of these pseudo-components are assumed to exist in the solution, and an equilibrium will be

[1] Smits, Versl. Kon. Akad. v. Wet., **22**, 642 (1913); **27**, 1 (1918); **27**, 981 (1919); **27**, 1470 (1919).

Smits and Aten, *Z. physik. Chem.*, **90**, 723 (1915); **92**, 1 (1916).

Smits and Byvoet, Versl. Kon. Akad. v. Wet., **27**, 311 (1918).

For a complete development of the theory, see Smits, *The Theory of Allotropy*. English Translation. Longmans, Green & Co. (1922).

established between the two phases which will be represented by

$$\begin{array}{ccccc} Me_s & \rightleftharpoons & Me_s^{\nu+} + \nu\Theta_s, \\ \updownarrow & & \updownarrow & & \updownarrow \\ Me_l & \rightleftharpoons & Me_l^{\nu+} + \nu\Theta_l, \end{array}$$

where the symbols with the subscript l refer to the solution. Such an equilibrium requires the equality of the partial free energies, or activities of each pseudo-component in the solid and liquid phases. Smits has employed this equation to represent the electrode equilibrium, and, on this basis, has developed mathematical equations for reversible electrode potentials, concentration cells, etc. Some metals may have a greater phase complexity than above represented. For example, the pseudo-components of iron may be Fe^{++}, Fe^{+++}, Fe, and Θ.

When stable equilibrium exists between the pseudo-components in the metal, in the solution, and between the metal and the solution, the electrode will be reversible and its potential will have its corresponding value. If, on the other hand, the inner equilibrium of the system be disturbed by electrolysis, or by some chemical means, the potential may vary far from its normal value. This will also be the case if the inner equilibrium of the metal surface be displaced. On removing the disturbing cause, the potential will return to its normal value as inner equilibrium is again established. This latter process may take place with different degrees of rapidity and may depend on the presence of positive and negative catalysts.

INTRODUCTION TO ELECTROLYSIS AND POLARIZATION PHENOMENA

Imagine the electromotive force of a galvanic cell to be exactly balanced at a given instant by a constant external electromotive force. The cell will be reversible if every substance composing it is in a stable state, and if a very small increase in the applied external electromotive force will cause reactions which will be exactly reversed by a very small decrease in the external electromotive force. As long as these conditions prevail, the electromotive force of the cell will remain constant, and will correspond to the free energy decrease of the cell reaction.

If, on the contrary, any actual process brought about by chemical reaction or by electrolysis is taking place in the cell, the system will be undergoing an irreversible change and its electromotive force will vary with the time. In the following discussion, such irreversible changes produced at electrodes by electrolysis will be considered.

Electrolysis and Reversible Electrode Potentials, Counter Electromotive Force, Decomposition Potential, Polarization, and Overvoltage: Let **E** represent the electromotive force of the cell

$$Pt\,|\,H_2\ (1\ atm.)\,|\,HCl\ (m)\,|\,Cl_2\ (1\ atm.)\,|\,Pt$$

of which the cell reaction is

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 = HCl\ (m).$$

E is measured by balancing as nearly as possible with an opposing external electromotive force, whereby only a very small current passes in either direction through the cell. The reverse of the above reaction represents the electrolysis of the solution, from which it at once becomes apparent that in order to electrolyze the solution between platinum electrodes, an electromotive force, e,

greater than **E** must be applied. Under these conditions, **E** is a counter electromotive force, and is equal to the decomposition potential of the electrolyte, or the minimum electromotive force which must be applied in order to produce electrolysis.

During electrolysis, then, according to Ohm's law, we have

$$e - \mathbf{E} = CR, \tag{1}$$

where C is the current and R the resistance of the system. If e is only very slightly greater than **E**, the current density, or the current per unit of electrode area, will be very small and **E** will very nearly equal the reversible electromotive force of the cell. When e is considerably greater than **E**, and, consequently, the current density higher, considerable electrolysis will take place, which will produce physical and chemical changes in the system, and cause **E** to vary from its reversible value. Under these conditions, the cell and the cell electrodes are said to have undergone polarization. In general, polarization is any change produced at an electrode by electrolysis or by some other means which causes its potential to differ from its reversible or normal value.

The difference between the potential of an electrode which has undergone polarization and its reversible electrode potential in a solution of the same concentration of electrolyte we shall denote as the "overvoltage" of the electrode. Thus, the overvoltage of the hydrogen electrode in the above cell would equal the electromotive force of the irreversible cell

$$\mathrm{Pt}\,|\,\mathrm{H_2}\ (\text{depositing})\,|\,\mathrm{HCl}\ (m)\,|\,\mathrm{H_2}\ (\text{reversible})\,|\,\mathrm{Pt}.$$

Concentration Polarization: In all measurements of the electromotive force of reversible cells, so little current is allowed to flow that any concentration changes in the neighborhood of the electrodes are negligible. If, on the other hand, a considerable flow of electricity takes place either by discharging or charging the cell, concentration changes will take place in the neighborhood of the electrodes which may considerably alter the electromotive force of the cell. If the electrolyte is not stirred, these concentration changes can only be adjusted by the slow process of diffusion of the electrolyte.

At the beginning of the electrolysis of a copper sulphate solution between copper electrodes, the counter electromotive force is zero since the electrode potentials of the anode and cathode are equal. In order to electrolyze the solution, the applied electromotive force would only have to be sufficient to overcome the resistance of the solution. During electrolysis the copper ion concentration at the anode and at the cathode will increase and decrease, respectively. The net effect will be the production of a counter electromotive force equal to that of the concentration cell produced by the electrolysis. This counter electromotive force will be greater the greater the current density; it can be much reduced or eliminated by stirring.

When charged, the lead accumulator is

$$\mathrm{Pb}\,|\,\mathrm{PbO_2}\,|\,\mathrm{H_2SO_4}\ (m)\,|\,\mathrm{Pb}$$

and when completely discharged it is

$$Pb\,|\,PbSO_4\,|\,H_2SO_4\ (m')\,|\,PbSO_4\,|\,Pb.$$

The cell reaction [1] has usually been thought to be

$$Pb + PbO_2 + 2H_2SO_4\ (m) = 2PbSO_4 + 2H_2O.$$

A lead accumulator containing 20.9 per cent sulphuric acid has a normal electromotive force of 2.010 volts at 15°. On charging the partially discharged cell, its electromotive force rapidly rises to 2.1 volts, then more slowly to 2.2, and then rapidly to 2.6. If the cell is then allowed to stand without charging, its electromotive force soon changes to its normal value. During discharging, the electromotive force drops rapidly to 1.9, then slowly to 1.8 volts, and finally decreases more rapidly. If left undisturbed, the electromotive force rapidly rises to its normal value of 2.01 volts. These observations are due to Dolezalek[2] who has made a very comprehensive study of this cell. These variations of the electromotive force from its normal value are supposed to be almost if not entirely caused by concentration polarization. Sulphuric acid accumulates at both electrodes during charging and the process of diffusion is retarded by the porous lead dioxide.

Decomposition Potentials at Low Current Densities: In general, when a solution is placed between two platinum electrodes and an external voltage applied, a small current is first produced which drops and remains almost at zero until the decomposition potential is reached, and then, if the applied electromotive force be increased further, electrolysis will take place and the current will thereafter increase proportionally to the applied electromotive force. Under these conditions, the decomposition potential is equal to the counter electromotive force of the reversible or irreversible cell made up of the solution, the electrodes, and the products of the initial electrolysis.

Decomposition potentials may be measured by determining the break in the curve obtained by plotting the applied electromotive force against the current, or electrolyzing the solution by a definite external potential until the electrodes are charged with the decomposition products of electrolysis, interrupting this circuit, and then short circuiting the electrodes through a high resistance circuit containing a voltmeter or a high resistance potentiometer.

The principal investigations of decomposition potentials of acids, bases, and salts, in aqueous solutions, between platinum electrodes, and at low current densities, were made by Le Blanc.[3] Table XVI contains some of the values for normal salt solutions.

[1] That this may not be the correct cell reaction has been suggested by Fery, *J. Phys.*, 6, 21 (1916). See also MacInnes, Adler, and Joubert, *Trans. Am. Electrochem. Soc.*, 37, 641 (1920).

[2] Theory of the Lead Accumulator. English Translation by von Ende. Wiley & Sons, (1910).

[3] *Z. physik. Chem.*, 8, 299 (1891); Text-book of Electrochemistry, Le Blanc. English Translation by Whitney and Brown.

TABLE XVI

Decomposition Potentials of Normal Salt Solutions

Electrolyte	Decomposition Potential (volts)	Electrolyte	Decomposition Potential (volts)
$ZnSO_4$	2.35	$NiCl_2$	1.85
$NiSO_4$	2.09	$ZnBr_2$	1.80
$CdSO_4$	2.03	$CoCl_2$	1.78
$Cd(NO_3)_2$	1.98	$Pb(NO_3)_2$	1.52
$CoSO_4$	1.92	$AgNO_3$	0.70
$CdCl_2$	1.88		

At the cathode, the counter electromotive force will be produced by the boundary of the deposited metal and its ions, and will correspond to the reaction, $Me = Me^{\nu+} + \nu\Theta$. The anode reactions are more complicated and obscure. At very low current densities, if the metal is deposited in a stable condition, the counter electromotive force at the cathode should equal the reversible electrode potential of the metal. Under these ideal conditions, the decomposition potential is a minimum. That this is roughly the case for the above experimental results may be seen from the following examples. The difference between the decomposition potentials of zinc and cadmium sulphate is 0.32 volt while the difference between the molal electrode potentials of zinc and cadmium is 0.36 volt; and the difference between the decomposition potentials of cadmium and silver nitrates is 1.28 volts while the difference between the molal electrode potentials of cadmium and silver is 1.20 volts.

The decomposition potentials between platinum electrodes of some acids and bases as determined by Le Blanc are given in Table XVII.

TABLE XVII

Normal Decomposition Potentials of Acids and Bases

Electrolyte	Decomposition Potential (volts)	Electrolyte	Decomposition Potential (volts)
H_2SO_4	1.67	HCl	1.31
HNO_3	1.69	HI	0.52
H_3PO_4	1.70	NaOH	1.69
$CH_2ClCOOH$	1.72	NH_4OH	1.74
$HClO_4$	1.65	$N(C_2H_5)_4OH$ (0.125M)	1.74

There is much less variation in the decomposition potentials of most acids and bases than in those of the salts. Most of the values were found to be between 1.65 and 1.75 volts. Le Blanc pointed out that those acids and bases with a decomposition potential in the neighborhood of 1.70 volts deposited hydrogen and oxygen at the electrodes, and that 1.70 volts equalled approximately the decomposition potential of water on platinum electrodes. The potential of the reversible oxygen-hydrogen cell is about 1.2 volts. The difference between this and 1.7 volts is caused by polarization effects. The decomposition potentials of normal hydrochloric and hydriodic acids are nearly equal to the electromotive forces of the reversible cells

$$Pt \mid H_2 \mid HCl\ (M) \mid Cl_2 \mid Pt$$

and

$$Pt\,|\,H_2\,|\,HI\ (M)\,|\,I\ (s)\,|\,Pt,$$

which are 1.36 and 0.53 volts, respectively. In normal solutions of these acids, therefore, chlorine and iodine are deposited. Le Blanc found that if the hydrochloric acid solution be diluted, its decomposition potential will increase, and hydrogen and oxygen will be evolved. Thus, a 0.03N hydrochloric acid solution was found to have a decomposition potential of 1.69 volts.

Cathode Potentials during Metal Deposition: The magnitude of the variation of the electrode potentials of metals with a change in current density differs considerably with the different metals. In Table XVIII are given

TABLE XVIII

CATHODE POTENTIALS OF METALS AT DIFFERENT CURRENT DENSITIES

Current Density $\left(\frac{10^{-4}\text{ amperes}}{\text{Cm.}^2}\right)$	Cathode Potentials			
	$CuSO_4$	$FeSO_4$	$NiSO_4$	$CoCl_2$
0	− 0.303	0.465	(0.220)	0.290
1	− 0.294	0.580	0.445	0.370
5	− 0.285	0.619	0.524	0.415
10	− 0.275	0.630	0.546	0.430
20	− 0.270	0.645	0.559	0.440
40	− 0.260	—	0.570	0.459
80	− 0.240	—	0.590	0.495

some values of the cathode potentials at round current densities, read off plots of the results of Foerster and his collaborators.[1] These potentials are referred to the normal hydrogen electrode, and were determined at 20°. All the salt solutions were normal. The copper sulphate solution contained 0.01 normal sulphuric acid, and the other salt solutions contained 0.5 per cent of boric acid.

The variation of the electrode potential of copper is very much less than that of the metals of the iron group. Further confirmation of this point is found in some more recent determinations of metal overvoltage. According to the definition, the metal overvoltage during metal deposition will equal the electromotive force of the cell

$$\text{Me (depositing)}\,|\,Me^{\nu+}\,|\,\text{Me (reversible)}.$$

Newbery,[2] by employing an intermittent, instead of a direct, current, obtained 0.02, 0.00, 0.02, 0.00, 0.01, 0.02, 0.82, 0.30, 0.46, for the overvoltages of copper, silver, zinc, lead, cadmium, thallium, nickel, iron, and cobalt, respectively, at a current density of 100 milliamperes per sq. cm.

One plausible explanation of this behavior, employed by Foerster, is that the electrode process, $\frac{1}{2}Me^{\nu+} + \nu\Theta \rightarrow \frac{1}{2}Me$, proceeds more slowly in the cases

[1] Foerster, Abh. Deutsch. Bunsengesellschaft. No. 2 (1909); Schweitzer, *Z. Elektrochem.*, **15**, 602 (1909).

[2] Mem. Proc. Manchester Lit. Phil. Soc. 61, Parts II and III, Mem. No. 9 (1917).

where there is a high degree of polarization. Such a retardation would set up a potential opposite in direction to the external electromotive force, and, consequently, a higher applied electromotive force would be required in order to produce the same current density.

Much more pronounced polarization effects are observed when a metal is deposited from a solution of a complex compound than from a solution of a simple salt. A solution containing a complex ion such as $Cu(CN)_2^-$ would contain few Cu^+, and these would be removed almost immediately by electrolysis. The electrode potential might then depend on the rate at which the complex ion decomposed into the metal ion. The slower this velocity, the greater would be the polarization, and the more pronounced the observed change in cathode potential.

Nature of Metallic Deposits: The physical state of electrolytically deposited metals varies widely with the nature of the electrolyte, the current density, and other factors. By varying the conditions of electrolysis, the same metal may be deposited in a crystalline form or in the condition of a spongy mass. The difference of potential between two electrodes of the same metal in such different physical states in a solution of a salt of the metal may be as high as a few tenths of a volt.

That this is true has been shown by numerous investigators. Lewis and his associates have shown that the most reproducible metal electrodes are those of the alkali metals. Lewis and Brighton [1] found that sticks of lead six years old had the same potential as a lead tree freshly precipitated by electrolysis. Lewis and Lacey [2] found that finely divided electrolytically precipitated copper gave reproducible results. On the other hand, the potential of iron in different states of division differed very considerably.[3] Reproducibility of the iron potential may be obtained by employing a finely divided metal. Similar phenomena have been observed in the case of the nickel electrode.[4] Lewis and Brighton conclude "that the lack of reproducibility in electrodes of solid metal is due solely to conditions of strain in the solid surface. In the case of metals which flow readily, like lead, or sodium, or potassium, these accidental strains almost immediately disappear and the solid metals form entirely reproducible electrodes."

If a metal is deposited in a highly strained condition, it will tend to change into a more stable form, or tend to contract. This phenomenon is therefore closely associated with the peeling of electrolytically deposited metals. That there is a tendency for such deposits to contract has been strikingly shown by Kohlschütter and Vuilleumier,[5] and Vuilleumier,[6] who measured the degree of contraction of electrolytically deposited metals by means of a contractometer

[1] *J. Am. Chem. Soc.*, **39**, 1906 (1917).

[2] *J. Am. Chem. Soc.*, **36**, 804 (1914).

[3] Richards and Behr, *Z. physik. Chem.*, **58**, 301 (1907).

[4] Euler, *Z. anorg. Chem.*, **41**, 93 (1904); Schoch, *Am. Chem. J.*, **41**, 208 (1909); Schweitzer *Z. Elektrochem.*, **15**, 607 (1909).

[5] *Z. Elektrochem.*, **24**, 300 (1918).

[6] *Trans. Am. Electrochem. Soc.*, **42**, 99 (1922).

devised by them. This instrument consists of a thin platinum foil cathode to which is attached a glass pointer 30 cms. in length. The metal is deposited on one side of the foil, and, when contraction of the metal takes place, the foil is bent, and the movement of the point read off the scale. Definite contraction of the metals was observed. The contraction effect was relatively small for copper and silver, and large for nickel and iron. These facts are in agreement with the conclusion of Lewis and Brighton, according to which very little contraction would be observed in the cases of electrolytically deposited soft metals such as lead, sodium, or potassium.

Overvoltage of Hydrogen: In accord with previous considerations, we may define the overvoltage of hydrogen as the difference of potential between a reversible hydrogen electrode and an electrode in the same solution upon which hydrogen is being deposited from hydrogen ions. The overvoltage will equal the electromotive force of the cell

$$\text{Me } (H_2 \text{ depositing}) \,|\, H_2SO_4 \qquad \text{or} \qquad \text{NaOH, etc.} \,|\, H_2 \text{ (reversible)} \,|\, \text{Pt}$$

and will be positive.

There has been considerable controversy recently in regard to the correct method of measuring hydrogen overvoltage. In the earlier work of Caspari,[1] Tafel,[2] Müller,[3] and others, the overvoltage was measured while a continuous current electrolysis was taking place. Newbery,[4] who has made the most extensive investigation of overvoltage, has employed a rotating commutator by means of which the applied voltage circuit as well as the reference electrode circuit breaks and makes about 2,500 times a minute. Results obtained by the commutator and intermittent current are invariably lower than those obtained by the continuous current method. That this is the case may be seen from the results in Table XIX, taken from a recent investiga-

TABLE XIX

HYDROGEN OVERVOLTAGES FROM *N*-SULPHURIC ACID

Amperes 10^{-3} / Cm.^{2}	C.C.	I.C.	N.
	Lead		
150	1.23	1.05	0.56
50	1.18	1.01	0.64
10	1.11	0.98	0.71
	Nickel		
150	0.49	0.39	0.19
50	0.39	0.33	0.18
10	0.33	0.28	0.18

[1] *Z. physik. Chem.*, **30**, 89 (1899).

[2] *Ibid.*, **50**, 641 (1905).

[3] *Ibid.*, **65**, 226 (1909).

[4] Newbery, *J. Chem. Soc.*, **105**, 2419 (1914); **109**, 1051 (1916); **109**, 1066 (1916); **109**, 1107 (1916); **109**, 1359 (1916); **111**, 470 (1917); **119**, 477 (1921); **121**, 7 (1922); Mem. Proc. Manchester Lit. Phil. Soc., 61, Parts II and III, Mem. No. 9 (1917).

tion of Glasstone.[1] Three series of results are given, the first series (C.C.) are for a continuous current; the second (I.C.) are for a nearly perfect unidirectional intermittent current, obtained by employing a rectifier and bulb, and corresponding to a commutator making 3600 revolutions a minute; and the third (N) are those obtained by Newbery.[2] The first column gives the current density in milliamperes per sq. cm.

Newbery contends that the true counter electromotive force is only measured by the commutator method, and that when a continuous current is employed a film of hydrogen is formed at the electrode which cannot diffuse away, and which causes an electric resistance, called "transfer resistance," to the flow of the current. This transfer resistance is thought to be the cause for the difference between the electromotive forces measured by the two methods. The transfer resistance varies greatly with change in current density, and is of physical origin. The electromotive force measured by the commutator method is the true chemical overvoltage, and varies little as a rule with change in current density. This point of view has also been adopted by Sand, Weeks, and Worrell.[3]

The existence of any appreciable transfer resistance at low current densities has been questioned by MacInnes,[4] Dunhill,[5] and others,[6] who attribute the observed difference to a potential which rapidly decreases when the current is interrupted. Glasstone ascribes the difference in electromotive forces measured by the two methods partially to an alternating induced current set up by the make and break of the intermittent current. It is well known that an alternating current superimposed on a direct current lowers the overvoltage at gas electrodes.[7]

Although considerable confusion arises from these experimental difficulties, it is possible, by measuring overvoltages by one experimental method, to arrive

TABLE XX

Characteristic Overvoltage Data at Different Current Densities

Current Density	N-H_2SO_4				N-NaOH		
	Zn	Ni	Ir (*a*)	Ir (*b*)	Ni	Zn	Ir
2	0.68	0.16	0.01	0.18	0.18	0.59	0.43
10	0.69	0.18	0.03	0.18	0.20	0.60	0.44
50	0.71	0.18	0.04	0.18	0.21	0.59	0.44
100	0.71	0.19	0.05	0.18	0.21	0.59	0.45
1000	0.72	0.17	0.05	0.14	0.21	0.56	0.64
2000	0.72	0.15	0.08	0.12	—	—	0.63

[1] Glasstone, *J. Chem. Soc.*, **123**, 1745 (1923).
[2] *J. Chem. Soc.*, **109**, 1051 (1916); **109**, 1066 (1916).
[3] *J. Chem. Soc.*, **123**, 456 (1923).
[4] *J. Am. Chem. Soc.*, **42**, 2233 (1920).
[5] *J. Chem. Soc.*, **119**, 1081 (1921).
[6] Tartar and Keyes, *J. Am. Chem. Soc.*, **44**, 557 (1922).
[7] Grube and Dulk, *Z. Elektrochem.*, **24**, 237 (1918); Goodwin and Knoble, *Trans. Am. Electrochem. Soc.*, **37**, 617 (1920).

at some important but approximate conclusions regarding the relative overvoltages at cathodes of different elements (principally metals). If the commutator method be employed, Newbery found that, in the majority of cases, the overvoltage varied remarkably little for a change in current density from 2 to 2,000 milliamperes per sq. cm. cathode surface, while the direct current method gave very large variations. In Table XX are given a few characteristic measurements of hydrogen overvoltage at different current densities taken from Newbery's compilation.[1]

The values of the overvoltage of hydrogen on both zinc and nickel are roughly the same in both the sulphuric acid and sodium hydroxide solutions. This was found to be the case with the many other electrodes examined. The results with iridium cathodes are particularly interesting. The four distinct values, 0.18, 0.06, 0.45, and 0.67, were found by Newbery. The same phenomenon was observed in the case of electrodes of other elements which possess more than one valence. The direct current method does not give these discontinuities. Table XXI contains the hydrogen overvoltages for all the elements measured by Newbery arranged according to the groups of the periodic system.

TABLE XXI

Hydrogen Overvoltages of Elements

Group	Element	Overvoltages		
I	Cu	0.34		
	Ag	0.30		
	Au	0.36	(0.42)	
II	Mg	0.70		
	Zn	0.72		
	Cd	0.66	(0.50)	
	Hg	0.70	(0.53)	
III	Al	0.50	(0.19)	
	Tl	0.52		
IV	C (graphite)	0.35	(0.64)	
	Sn	0.45	(0.66)	
	Pb	0.42	(0.69)	
V	Sb	0.43	(0.67)	
	Ta	0.42		
	Bi	0.42	(0.76)	
VI	Cr	0.38		
	Mo	0.32		
	W	0.30		
VII	Mn	0.33	(0.57)	
VIII	Fe	0.27	(0.35)	
	Ni	0.24		
	Co	0.26	(0.69)	
	Rh	0.02	(0.08)	
	Pd	0.07	(0.58)	
	Ir	0.18	(0.04)	(0.45) (0.67)
	Pt	0.18	(0.06)	(0.45) (0.65)

The values which are not in brackets are taken by Newbery to be the principal overvoltage of the group, while the others are secondary. Each group of the periodic

[1] *J. Chem. Soc.*, **109**, 1051 (1916); **109**, 1107 (1916).

system has its definite overvoltage, a result which is hardly fortuitous, and which, as pointed out by Newbery, seems to link the overvoltage of hydrogen with the valence of the element employed as cathode.

Theories of Hydrogen Overvoltage: Many theories have been proposed to account for hydrogen overvoltage. These theories may be divided into three classes, which in turn attribute the cause of hydrogen overvoltage to purely physical factors, to chemical changes on electrodes, and to the velocity of electrode processes.

Let us first consider the purely physical factors which have been regarded either partially or completely to determine the overvoltage. Haber [1] proposed that the phenomenon is caused by a poorly conducting hydrogen layer of varying thickness. In more recent studies, such a layer is thought by some investigators to produce a "transfer resistance" but not to account for all the overvoltage. Müller [2] found that overvoltage depends on bubble formation. That this is the case, to some extent at least, during continuous current electrolysis has been interestingly shown by MacInnes and Adler [3] who determined the overvoltage of hydrogen on platinized platinum at very low current densities. They noticed a distinct periodicity of the overvoltage, which rose and fell between the limits of 1.6 and 1.9 millivolts, as the electrolysis proceeded. Every time that the overvoltage reached 1.9 millivolts, a bubble had separated at one point on the electrode leaving a small nucleus. As this nucleus grew in size, the voltage dropped, and then rose rapidly when the bubble again separated. Each rise and fall was associated with the formation and evolution of a single bubble. It is a matter of considerable importance that the formation of a minute bubble can determine the potential of an electrode many thousand times the area of the bubble.

On equating the molal electrical energy, obtained from the electromotive force measurement, with the energy necessary to form one mol of hydrogen bubbles of radius r, MacInnes and Adler obtained the equation

$$\mathbf{E} = \frac{6RT}{pr\mathbf{F}}\gamma,$$

where $\mathbf{E}$ is the overvoltage, p the pressure, γ the surface tension, the other symbols having their usual significance. They determined the bubble radius by a microscopic method, and found that the values of $\mathbf{E}$, calculated by the above equation, agreed approximately with the observed results. The effect of pressure on the overvoltage could also be predicted by means of this equation.

As a result of this investigation, MacInnes and Adler [4] have proposed the theory that hydrogen overvoltage is caused by a layer of supersaturated solution of dissolved hydrogen in the immediate neighborhood of the electrode. If an electrode adsorbs hydrogen, this layer cannot reach a high degree of

[1] *Z. Elektrochem.*, **8**, 539 (1902).
[2] *Z. physik. Chem.*, **65**, 226 (1909).
[3] *J. Am. Chem. Soc.*, **41**, 194 (1919).
[4] Also MacInnes and Contieri, *J. Am. Chem. Soc.*, **41**, 2013 (1919).

supersaturation and the overvoltage will be low. Metals which do not adsorb hydrogen readily will have a high overvoltage.

Other factors of a physical nature have been found which may influence the hydrogen overvoltage to an unknown extent. For instance, Newbery found that electrodes after prolonged use as cathodes exhibited rough surfaces on microscopic examination. Tiny craters were formed on the surface, a fact which indicated that the hydrogen entered the metal, developed a high pressure, and produced surface disintegration. Any increase in pressure of the hydrogen in or on the electrode would increase the overvoltage. Further, the gas which escapes during electrolysis is ionized. Newbery suggested that the ionized gas probably produces an electromotive force by induction. His investigation of this effect indicated that this electromotive force was opposite in sign to the overvoltage.

There is only one chemical theory of hydrogen overvoltage. Newbery contends that hydrogen overvoltage, (the true counter electromotive force, after the effects caused by transfer resistance, etc., have been eliminated), is primarily caused by the formation of unstable hydrides of high electrical conductivity on the electrode surfaces. The overvoltage corresponds to the free energy of formation of these hydrides. The nature of the hydride depends on the valence of the element employed as cathode. Multivalent elements have more than one hydride, and, consequently, have more than one overvoltage. This explains the dependence of overvoltage on valence, which is illustrated in Table XXI. As further evidence of this theory, Newbery points out that stibine may be formed at an antimony cathode by electrolysis of both sulphuric acid and sodium hydroxide solutions. Under similar conditions, hydrocarbons form at a carbon cathode. The formation of stibine under these conditions has been recently investigated comprehensively by Sand, Weeks, and Worrell.[1] Some evidence was likewise obtained by Newbery for the existence of hydrides at some metallic electrodes such as magnesium, cadmium, and copper. In connection with this theory, it is possible that the electrolysis might produce an adsorbed layer of hydrogen atoms, orientated on the electrode surface. In other words, the "hydrides" would not necessarily have to be in a truly molecular condition.

Many theories have been proposed which assign the cause of overvoltage to the retardation of electrode processes. If we suppose that the reaction

$$H^+ + \ominus \rightarrow \tfrac{1}{2}H_2$$

represents the electrode process, it is clear that any factor which would retard this reaction would increase the overvoltage. Nernst[2] suggested that such a retardation would be effected by the slowness with which an electrode which had adsorbed the gas could come in equilibrium with the surroundings.

[1] *J. Chem. Soc.*, **123**, 456 (1923).

[2] *Ber.*, **30**, 1547 (1897).

According to Bancroft [1] and Bennett and Thomson,[2] monatomic hydrogen is formed during the process, which combines to form molecular hydrogen according to the mechanisms

$$(1)\quad H^+ + \Theta \rightarrow H \qquad \text{and} \qquad (2)\quad 2H \rightarrow H_2.$$

If reaction (2) is slow, hydrogen atoms will accumulate and give rise to a greater counter electromotive force. It is possible that the metal electrodes might have specific catalytic effects on these reactions, thus producing different overvoltages. Rideal [3] has suggested another theory of these processes. Monatomic hydrogen is first formed but immediately reacts to form molecular hydrogen. Overvoltage is a measure of the free energy or work necessary to remove the molecular hydrogen from the metal surfaces.

Smits' Theory of Polarization Phenomena: The application of Smits' theory of electromotive equilibria to polarization phenomena differs to a considerable extent from any of the theories just discussed. Indeed, Smits explains cathode polarization and anode polarization of metals and gases in general by postulating a disturbance of the inner equilibrium of the metal or gas phase.

Let us first consider what may occur at the cathode and anode when, for example, a solution of copper sulphate is electrolyzed between electrodes of copper. To simplify matters, let it be assumed that the copper ion concentration remains the same throughout the solution. Before electrolysis takes place, the heterogeneous equilibrium at each electrode surface will be

$$\begin{array}{ccc} Me_s & \rightleftharpoons & Me_s^{\nu+} + \nu\Theta_s, \\ \Updownarrow & & \Updownarrow \quad \Updownarrow \\ Me_l & \rightleftharpoons & Me_l^{\nu+} + \nu\Theta_l. \end{array}$$

Smits assumes that the heterogeneous equilibria, $Me_s \rightleftharpoons Me_l$, $Me_s^{\nu+} \rightleftharpoons Me_l^{\nu+}$, and $\nu\Theta_s \rightleftharpoons \nu\Theta_l$, will always be established instantaneously. During electrolysis, electrons will be supplied to the cathode from the external circuit, and metallic ions will be deposited. Metal atoms will form according to the scheme:

$$\begin{array}{ccc} & & \nu\Theta \\ & & \downarrow \\ Me_s^{+} & + & \nu\Theta_s \rightarrow Me_s. \\ \uparrow & & \\ Me_l^{\nu+} & & \end{array}$$

If the homogeneous reaction

$$Me_s^{\nu+} + \nu\Theta_s \rightarrow Me_s$$

takes place so rapidly that $\nu\Theta_s$ disappears to form Me_s as rapidly as $\nu\Theta$ enters the cathode, the inner equilibrium concentrations will be maintained, and the potential of the electrode will not change. But, if this latter reaction takes

[1] *J. Phys. Chem.*, **20**, 396 (1916).
[2] *Ibid.*, **20**, 296 (1916); *Trans. Am. Electrochem. Soc.*, **29**, 24 (1916).
[3] *J. Am. Chem. Soc.*, **42**, 94 (1920).

place slowly, then the metal surface will contain an excess of electrons and ions, and $Me_s^{\nu+}$ will be greater than $Me_l^{\nu+}$. The electrode will then possess a greater tendency to give off ions and its potential will be more positive. We have already found that metals such as iron, cobalt, and nickel, when deposited electrolytically, have a higher potential than in the normal state. Indeed, the overvoltage of these metals was found to be a function of their physical state, which would in turn depend on the extent to which the inner state of the system is displaced from the stable equilibrium state. According to the theory of Smits, the above homogeneous solid reaction would be slow in the cases of iron, cobalt, and nickel, and rapid for copper, lead, etc.

Just the opposite occurs at the anode where electrons are drawn into the external circuit. The anode process will be

$$\begin{array}{c} \nu\Theta \\ \uparrow \\ Me_s^{\nu+} + \nu\Theta_s \leftarrow Me_s. \\ \downarrow \\ Me_l^{\nu+} \end{array}$$

If Me_s will supply electrons as rapidly as they are removed, polarization will not occur. If the reaction

$$Me_s \rightarrow Me_s^{\nu+} + \nu\Theta$$

is slow, the anode surface will contain less electrons and ions than correspond to inner equilibrium, and the metal to solution electrode potential will become more negative. These homogeneous reactions may be influenced by catalysts. The presence of oxygen gas, according to Smits, retards, the presence of hydrogen gas or the chloride ion accelerates this last reaction.

The electrolytic overvoltage of hydrogen is due to the same cause as metal cathode overvoltage. In depositing hydrogen, the homogeneous reaction in the gas phase

$$2H_g^+ + 2\Theta_g \rightarrow H_{2g}$$

takes place. If this reaction does not occur as rapidly as electrons are supplied, the gas will contain more ions and electrons than under inner equilibrium conditions. As with metal deposition, since H_g^+ will be greater than H_l^+, the hydrogen electrode potential corresponding to such a disturbance will be more positive.

Anodic Overvoltage during Gas Deposition: The phenomenon of overvoltage which was found to occur during the deposition of hydrogen and metals likewise occurs during the deposition of other gases. The overvoltage of chlorine from normal hydrochloric acid will equal the electromotive force of the cell

$$Me\ (Cl_2\ depositing)\,|\,HCl\ (N)\,|\,Cl_2\,|\,Pt; \qquad \mathbf{E} = \text{negative value},$$

where $Cl_2\,|\,Pt$ is the reversible chlorine electrode. Chlorine overvoltages have

recently been investigated by Newbery.[1] Carbon, rhodium, iridium and platinum are unattacked by the chlorine. Gold and palladium are attacked readily at low current densities. When higher current densities are employed (200 milliamperes per sq. cm. for gold and 50–100 milliamperes per sq. cm. for palladium), reaction of chlorine on the metal stops, chlorine gas is evolved freely, and the potential changes more than 0.5 volt. Under these conditions, the metals are in the "passive state" and are not attacked by the chlorine.

For the metals in the passive state or for the non-corrodible electrodes, Newbery found that the overvoltage of chlorine had the same value as the overvoltage of hydrogen. He concludes that chlorine overvoltage as well as hydrogen overvoltage is a function of the valence of the element. Platinum shows three distinct overvoltages which are 0.0, 0.18, and 0.45 volt. Intermittent current electrolysis was employed throughout this investigation.

The overvoltage of oxygen is equal to the electromotive force of the cell

$$\text{Me}(O_2 \text{ depositing}) \,|\, \text{NaOH or } H_2SO_4 \text{ etc.} \,|\, O_2 \,|\, \text{Pt}; \qquad \mathbf{E} = \text{negative value},$$

where $O_1|\,\text{Pt}$ is the reversible oxygen electrode. In Table XXII are given some of the values of oxygen overvoltages obtained by Newbery by the intermittent current method. The direct current method yields somewhat higher results.[2] Normal solutions of sodium hydroxide and sulphuric acid were employed.

TABLE XXII

Oxygen Overvoltages

Metal	Overvoltage = (− E)	Metal	Overvoltage = (− E)
Cu	0.62	Co	0.55
Ag	0.71	Pd	0.65
Zn	0.93	Ir	0.48
Pb	0.94	Pt	0.86
Ni	0.57	Mn	0.92

These anode overvoltages compared to the oxygen electrode are invariably higher than the hydrogen overvoltages in the case of a given metal electrode.

Passivity of Metals and Anodic Polarization: The fact that after iron is dipped into strong nitric acid it resists the action of dilute acids has been known for a long time.[3] The nitric acid changes the surface of the iron and renders it "passive." Ordinary or active iron possesses an electrode potential 0.390 volt more positive than copper and 0.845 volt more positive than silver, and, therefore, will replace both these metals from solutions of their salts. When iron becomes passive, its potential becomes more negative, or is changed in the direction of the potential of the noble metals. In the passive state, iron will not precipitate copper or silver from solutions of their salts. The same is true of cobalt, nickel, and chromium. If passive iron is washed with pure

[1] *J. Chem. Soc.*, **119**, 477 (1921).
[2] Glasstone, *J. Chem. Soc.*, **123**, 1745 (1923).
[3] Keir, *Phil. Trans.*, **80**, 374 (1790).

water, alcohol, and ether, and dried in the presence of air, it remains passive. In a vacuum, it becomes active. Passive iron has never been obtained in the absence of air.

Metals may be caused to lose their passivity in many ways. This may be most strikingly demonstrated by rendering passive, by dipping into strong nitric acid, a clean and well-polished sheet of iron, held by a glass hook. The surface is then covered with a copper sulphate solution by immersing in a solution of that salt. No copper will be precipitated. If any part of the metal be scratched with a piece of glass, copper will be precipitated at the scratch and the precipitation will proceed from the scratch over the entire surface very rapidly. A blow will bring about the same result. Contact with active iron, or any metal such as nickel, cobalt, or magnesium, which has a higher electrode potential, will produce the same result. Noble metals such as gold or platinum will not cause activation. As a matter of fact, their presence in contact with the iron is thought to help to induce passivity. The same type of phenomena occurs when a silver nitrate solution is employed instead of a copper sulphate solution. In this case, the activation spreads more slowly over the surface, and may be clearly seen to proceed from the areas disturbed by the contact. Nickel and cobalt behave in a similar manner.

Passive metals may be rendered active by contact with solutions containing halogen ions. Thus, if the tip of the passive iron sheet, covered with the copper sulphate solution, be immersed in a solution containing the chloride, bromide, or iodide ion, activation will proceed from the immersed part over the entire surface. Usually, in this case, there will be a short induction period, which is probably due to the time required for the halogen ions to diffuse through the copper sulphate solution. Passive metals are also rendered active by increase in temperature.

When certain metals are made the anode in acid or basic solutions, passivity is brought about by electrolysis, and when the change from the active to the passive form takes place, it is accompanied by a large increase in counter electromotive force. In some cases, it seems obvious that passivation is due to the formation of an oxide. Thus, lead passivates readily in acid solutions at low current densities, and at the same time becomes coated with a layer of the dioxide. At low current densities a silver anode remains active. A current density of 50 milliamperes per sq. cm. causes passivity and the counter electromotive force changes by more than a volt in a few seconds. If the current density be lowered to 20 milliamperes per sq. cm., the anode slowly regains its activity. At a current density of 40 milliamperes per sq. cm., a periodic rise and fall of the counter electromotive force is observable. In thirty seconds the rise is about 0.6 volt, and a corresponding fall takes place in about two and one half minutes.[1] In sulphuric acid solution nickel becomes passive at a current density of about 100 milliamperes per sq. cm. At 50 milliamperes there is a periodic change in the potential of the electrode. The potential changes about 1.1 volts and the period of fall or rise is about six seconds. When iron, cobalt, or nickel are rendered passive by electrolysis or by concentrated nitric acid, there is no visible change of appearance of the metallic surface.

Another interesting example of periodic passivation has been carefully investigated by Smits and de Bruyn[2] who used a photographic method to

[1] Newbery, *J. Chem. Soc.*, **109**, 1066 (1916).

[2] Versl. Kon. Akad. v. Wet. Amsterdam, **24**, 745 (1915); **27**, 159 (1918).

record the phenomenon. The electrolyte consisted of a solution containing ferrous, sulphate, and chloride ions. The chloride ions will render passive iron active, and the electrolysis will cause passivation. The net result is a periodic passivation and activation with a corresponding periodic change in anode potential of 1.74 volts. The duration of successive periods of fluctuation is about 6 seconds.

Theories of Passivity: Many investigators have supported the view that passivity is caused by the presence of an oxide film on the surface of the metal which is produced either by the chemical action of nitric acid or bichromate solutions, or by the oxidation of the anode. In order to account for the behavior of passive metals and the sign of the anode overvoltage, it must be assumed that these oxides are very unstable, spontaneously decomposable, and, consequently, unlike any of the known oxides of the metals. These considerations were employed by Hittorf [2] against the oxidation theory, since a passive metal will stay passive under favorable conditions over a time of considerable duration. We are dealing here, however, not with oxide alone but with oxide in intimate contact with a metallic surface. Stabilization of an unstable compound when adsorbed on a solid is a well-known phenomenon.[3] Bennett and Burnham have therefore regarded passivity as due to a layer of an oxide adsorbed on the metal. In the case of iron, the oxide may be FeO_2 or FeO_3, in the case of chromium, CrO_2, etc. Periodic changes of anode potentials would be explained by an alternate formation and removal of the oxide film.

Müller and Königsberger [4] showed that the reflecting power of active and passive iron was the same. They also showed that the presence of a film of lead dioxide of a thickness of 0.8 $\mu\mu$ changed the reflecting power of platinum to a very considerable extent. From these results the conclusion was drawn that passive iron was not coated with a film of oxide.

The theory that passivity is caused by the retardation of the heterogeneous process

$$Me_s \rightarrow Me_l^{\nu+} + \nu\Theta$$

has been supported in somewhat different ways by a number of investigators.[5] In the more recent of these theories, oxygen is regarded as a negative catalyst for this reaction, and hydrogen a positive catalyst in as much as the hydrogen removes the oxygen.

[1] Faraday, *Phil. Mag.*, (3) **9**, 122 (1836); Haber and Goldschmidt, *Z. Elektrochem.*, **12**, 49 (1906); Bennett and Burnham, *Trans. Am. Electrochem. Soc.*, **29**, 38 (1916); Newbery, *J. Chem. Soc.*, **109**, 1107 (1916); **109**, 1359 (1916).

[2] *Z. physik. Chem.*, **25**, 729 (1898); **30**, 481 (1899); **34**, 385 (1900).

[3] Bancroft, Applied Colloid Chemistry. McGraw-Hill Book Co. (1921), p. 122.

[4] *Physik. Z.*, **5**, 415 (1904); **5**, 497 (1904); **6**, 847 (1905); **7**, 797 (1906); **13**, 659 (1912).

[5] Le Blanc, *Z. physik. Chem.*, **6**, 472 (1900); Fredenhagen, *ibid.*, **43**, 1 (1903); **63**, 1 (1908); Foerster, Abh. Deutsch. Bunsengesellschaft. No. 2 (1909). See also section on Passivity in Foerster, Electrochemie wässeriger Losungen, Barth, Leipzig (1921), where a comprehensive résumé of the theories on this subject is given.

According to Smits' theory of electromotive equilibrium, we found that during anodic solution of a metal, if the homogeneous reaction

$$Me_s \rightarrow Me_s^{\nu+} + \nu\Theta_s$$

is slow, the metal surface will contain fewer electrons as a result of the disturbance than under inner equilibrium conditions, and the anode potential will be more negative. If the current density becomes sufficiently high, the disturbance caused by the electrolysis may reach such a magnitude as to change the anode potential until it reaches the electrode potential of oxygen and then oxygen will be deposited. According to Smits, oxygen is adsorbed somewhat at the anode and is a negative catalyst for the above reaction. Passivity is then caused by the removal of ions and electrons from the metal by making it the anode during electrolysis, or by dissolving in acids, thus producing displacement of the inner equilibrium of the metal. The system is held in this unstable state by the presence of a negative catalyst such as dissolved oxygen. Inner equilibrium is established less rapidly in iron, nickel, cobalt, and chromium than in copper, in consequence of which the former may be rendered passive.

Assuming that, up to the present point, this theory is correct, the question may be legitimately asked: How does oxygen retard the homogeneous solid reaction from metal to ions and electrons? The answer to this question might easily involve either an oxide layer or a monomolecular film of oriented oxygen atoms on the metallic surface.

General Remarks: The preceding brief discussion of the phenomena of overvoltage and passivity has indicated that up to the present time explanations of the cause of these behaviors are divided principally into two distinct types. The first attributes the cause to the formation of chemical substances on the electrodes. In such cases as the anodic passivity of lead, this point of view seems to be unquestionably valid, but in such cases as the anodic passivity of iron, the presence of an unstable compound cannot be regarded as established. The second theory takes these phenomena to be examples of irreversible processes, to depend on unstable physical states produced by electrolysis, and to be explained in terms of the velocities and catalytic acceleration or retardation of the electrolytic processes involved. Such a theory, although based on assumptions regarding the inner mechanism of the processes which must be regarded as highly conjectural, has been shown by Smits to be consistent with the laws of thermodynamics.

In this discussion of irreversible electrode processes, an attempt has been made to present the theories of the subject in an impartial manner. In this way, we are introduced to the varied literature of the subject. The conflicting opinions concerning the nature of overvoltage and passivity are in themselves an excellent proof of the obscurity which at the present time veils the true nature of the phenomena involved.

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